complete

PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. XVII. Nos. 231—244.
JANUARY—DECEMBER, 1901.

EDITED BY THE SECRETARIES.

LONDON
GURNEY & JACKSON, 1, PATERNOSTER ROW,
1902.

RICHARD CLAY AND SONS, LIMITED
LONDON AND BUNGAY

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£20 to G. D. Lander, to continue the study of the synthesis and properties of imino-ethers, and to extend the method of alkylation by silver oxide and alkyl iodides.

£20 to A. W. Crossley, to investigate the hydrolysis of substituted dihydroxyresorcinols.

£10 to H. Sand, to continue his research on changes of concentration at the electrodes in a solution of an organic compound in which no convection currents of the liquids take place.

Re-appropriation of balance of last grant to J. McCrae, to prepare and optically examine some amide derivatives of *l*-malic acid.

£5 to E. P. Perman, to continue his research on the vapour pressures of aqueous ammonia solution.

£5 to G. Dean, to investigate the action of bromine upon silver cyanate.

£5 to T. S. Patterson, to continue his research on the influence of solvents on the rotation of optically active compounds.

£15 to K. J. P. Orton and A. E. Garrod, to investigate the change of tyrosin into homogentisic acid and allied reactions.

£30 to J. J. Hummel and A. G. Perkin, to investigate the constitution of certain natural colouring matters.

£20 to W. A. Bone, to continue his investigations on alkyl substituted succinic and tricarballylic acids.

£5 to R M. Caven, to continue his investigation of the organic derivatives of phosphorus oxychloride, and for the investigation of amidines of the type OP(NHR)NR and the questions of tautomerism arising therefrom.

£5 to R. H. Pickard, to investigate the constitution of cholesterol.

£5 to R. H. Pickard, to investigate the condensation reactions of monosubstituted biurets, and the formation of ring compounds from these and the corresponding allophanates.

£5 to D. R. Boyd, to further investigate the aromatic ethers of glycerol.

£10 to J. B. Cohen, to investigate the law which determines substitution by chlorine and bromine in presence of a halogen carrier.

£25 to A. Lapworth, to investigate the oximes of hydroxy- and amido-camphor, and the intra-conversion of tautomeric forms.

£10 to A. E. Tutton, to continue his chemico-crystallographical investigation of the selenates.

£20 to J. Wade, to continue his investigation of the isocyanides as bearing on the constitution of hydrogen cyanide and the mechanism and conditions of isomeric change.

£10 to H. O. Jones, to further investigate certain cases of stereoisomerism and the causes which produce optical activity and govern the production of optically active substances.

£15 to A. W. Crossley and H. R. Le Sueur, to investigate substituted dihydrobenzenes.

£10 to W. H. Mills, for experiments on the synthesis of the hydrocarbons $C_{10}H_6\begin{<}{CMe \atop CH}\end{>}C_{10}H_6$ and $\begin{matrix} C_{10}H_6\cdot CMe \\ | \\ C_{10}H_6\cdot CH \end{matrix}$.

LIST OF FELLOWS ELECTED DURING 1901.

Name.	Proposed.	Elected.
Adams, Ormsby Gore	May 2nd, 1901	June 20th.
Aitken, Andrew Charles	December 6th, 1900	February 7th.
Allen, Frederick T., B.Sc.	November 7th, 1901.	December 5th.
Anderson, William C., M.A., D.Sc.	February 7th, 1901	May 2nd.
Ashwell, Guy	April 18th, 1901	June 20th.
Aspinall, Thomas	,, ,,	,, ,,
Aston, William George	,, ,,	,, ,,
Baker, Arthur	November 7th, 1901	December 5th.
Baker, Thomas Thorne	June 20th, 1901	,, ,,
Ball, Walter Craven, B.A.	November 7th, 1901	,, ,,
Barker, Hubert Haigh	May 16th, 1901	June 20th.
Barrie, Thomas Stewart	December 6th, 1900	February 7th.
Beaven, Edwin Sloper	April 18th, 1901	June 20th.
Bedford, Frederick	,, ,,	,, ,,
Bedwell, John Cardew, B.Sc.	December 6th, 1900	February 7th.
Bennet, Andrew Russell	November 7th, 1901	December 5th.
Bickford, Harding	,, ,,	,, ,,
Blake, George Stanford	February 7th, 1901	May 2nd.
Bolton, Edward Richards	,, ,,	,, ,,
Bousfield, Edward G. P.	February 21st, 1901	,, ,,
Boyers, Henry	November 7th, 1901	December 5th.
Bridges, Joseph Samuel, B.Sc.	May 2nd, 1901	June 20th.
Bult, Herbert John	December 6th, 1900	February 7th.
Burgess, Percival J., M.A.	January 17th, 1901	May 2nd.
Burrows, Merrick W., M.Sc.	December 20th, 1900	February 7th.
Burton, William, B.Sc.	November 7th, 1901	December 5th.
Carter, William	February 7th, 1901	May 2nd.
Clark, Ernest, B.Sc.	March 7th, 1901	,, ,,
Cockburn, Thomas Kennedy	,, ,,	,, ,,
Coddington, Eustace, B.A.	March 7th, 1901	May 2nd.
Cohen, Robert Waley, B.A.	December 20th, 1900.	February 7th.
Cormack, William	November 7th, 1901.	December 5th.
Cousins, Herbert H., M.A.	November 15th, 1900	February 7th.
Crabtree, Arthur	April 18th, 1901	June 20th.
Crocker, Walter Stevens	January 17th, 1901	May 2nd.
Crookes, Samuel Irwin	June 6th, 1901	December 5th.
Crossley, Frank	November 7th, 1901.	,, ,,
Dakin, Henry Drysdale	February 7th, 1901	May 2nd.
Daniel, Gilbert Howard, B.Sc.	December 6th, 1900	February 7th.
Davidson, John Howard, B.Sc.	November 7th, 1901	December 5th.
Davis, Francis	,, ,,	,, ,,
Dean, George, M.A.	May 16th, 1901	June 20th.
Dodd, Robert	November 15th, 1900.	February 7th.
Donnan, Frederick G., M.A., Ph.D.	December 6th, 1900	,, ,,
Dubois, Raymond, B.Sc.	January 17th, 1901	May 2nd.
Duckworth, William Henry	March 21st, 1901	,, ,,
Dunstan, Albert Ernest, B.Sc.	February 21st, 1901	,, ,,
Eastick, Samuel Philip	March 21st, 1901	,, ,,
Eling, Thomas H. J., B.A.	May 16th, 1901	June 20th.

Name.	Proposed.	Elected.
Ellis, Hugh Edward	March 7th, 1901	May 2nd.
Emery, John Alfred	December 6th, 1900	February 7th.
English, Robert	November 7th, 1901	December 5th.
Eyre, John Vargas	March 7th, 1901	May 2nd.
Ferguson, Reginald W.	December 20th, 1900	February 7th.
Gadd, Henry Wippell	November 7th, 1901.	December 5th.
Gajjar, T. K., M.A., B.Sc.	November 21st, 1901.	,, ,,
Gardner, Hermann Charles T.	November 7th, 1901.	,, ,,
Gillman, Edward	,, ,,	,, ,,
Groves, William Peer, B.A.	November 7th, 1901.	,, ,,
Haddon, Henry Edward	January 17th, 1901	February 7th.
Hammond, Herbert Blackmore	June 6th, 1901	December 5th.
Hanley, John	February 7th, 1901	May 2nd.
Hanson, Edward K., B.A.	May 16th, 1901	June 20th.
Harding, Herbert	November 7th, 1901.	December 5th.
Harrison, John A., B.Sc.	February 7th, 1901	May 2nd.
Harry, Frederick Thomas	May 16th, 1901	June 20th.
Henley, Francis R., B.A.	March 7th, 1901	May 2nd.
Higgs, Henry Herbert, B.Sc.	February 7th, 1901	,, ,,
Hobson, Edwin	June 20th, 1901	December 5th.
Horton, Edward	May 16th, 1901	June 20th.
Houldershaw, Arthur	November 15th, 1900.	February 7th.
Howard, Bernard Farmborough	December 6th, 1900.	,, ,,
Hughes, Edward	November 15th, 1900.	,, ,,
Hutton, Robert Salmon, M.Sc.	,, ,,	,, ,,
Hyder, Alfred James	February 21st, 1901	May 2nd.
Ingram, Beresford, B.A.	November 7th, 1901.	December 5th.
Ionides, Stephen Archigenes	November 15th, 1900.	February 7th.
Jameson, J. S.	November 21st, 1901.	December 5th.
Jemmett, William Henry C., B.A.	February 21st, 1901.	May 2nd.
Johnson, Charles H., M.B., Ch.M.	June 20th, 1901	December 5th.
Jollyman, Walter Henry	November 7th, 1901.	,, ,,
Jones, Major J. L. T., I.M.S.	December 20th, 1900.	February 7th.
Jones, Robert Henry, M.Sc.	November 15th, 1900.	,, ,,
Kettle, James David, B.Sc.	November 7th, 1901.	December 5th.
Kiddell, Christopher George	May 16th, 1901	June 20th.
Bruce-Kingsmill, J., M.A., B.Sc.	November 7th, 1901.	December 5th.
Larter, Alfred Tabois	,, ,,	,, ,,
Lattey, Robert Tabor, B.A.	May 16th, 1901	June 20th.
Leahy, Albert W. D.	November 21st, 1901.	December 5th.
Lehmann, Adolf L. F., B.Sc., Ph.D.	May 2nd, 1901	June 20th.
Lewis, Ernest Alfred	March 21st, 1901	May 2nd.
Linde, H. T. G. van der	November 15th, 1900.	February 7th.
Loewenthal, Oscar	January 17th, 1901	May 2nd.
Lowson, William, B.Sc.	May 2nd, 1901	June 20th.
Macdonald, F. G.	May 16th, 1901	,, ,,
Macdonald, Peter	November 7th, 1901.	December 5th.
Martin, Nicholas Henry	December 6th, 1900	February 7th.

Name.	Proposed.	Elected.
McKenzie, Alexander, M.A., Ph.D., D.Sc.	March 21st, 1901	May 2nd.
McLaren, Daniel, B.Sc.	April 18th, 1901	June 20th.
Mees, C. E. K.	March 7th, 1901	May 2nd.
Menzies, James	December 20th, 1900	February 7th.
Meredith, William	November 15th, 1900	,, ,,
Millard, Charles K., M.D., D.Sc.	November 7th, 1901.	December 5th.
Miller, Edward Holl	June 20th, 1901	,, ,,
Moir, James, M.A., B.Sc.	November 15th, 1900	February 7th.
Müller, Christian	June 6th, 1901	December 5th.
Murphy, Albert John	February 7th, 1901	May 2nd.
Neil, Arthur Theodore, B.A.	,, ,,	,, ,,
Neumann, Edgar, B.A., Ph.D.	March 21st, 1901	,, ,,
Newbould, Herbert Simpson	June 20th, 1901	December 5th.
Nunn, Arthur W.	December 20th, 1900	February 7th.
Oldershaw, William	March 21st, 1901	May 2nd.
Oram, Frank	May 16th, 1901	June 20th.
Page, Theodore Henry	December 6th, 1900	February 7th.
Parkes, Albert Edward	November 7th, 1901.	December 5th.
Pay, Walter Herbert	November 21st, 1901	,, ,,
Peacock, Arthur, B.Sc.	March 7th, 1901	May 2nd.
Pollitt, Charles James Tomlin	November 7th, 1901.	December 5th.
Potter, Rowland Samuel	June 6th, 1901	,, ,,
Powell, John, B.Sc.	April 18th, 1901	June 20th.
Price, Thomas Slater, Ph.D., D.Sc.	December 6th, 1900.	February 7th.
Purvis, John Edward, M.A.	May 16th, 1901	June 20th.
Radcliffe, Lionel Guy	December 6th, 1900.	February 7th.
Ramsden, William Cecil	,, ,,	,, ,,
Robertson, William	February 7th, 1901	May 2nd.
Robinson, William Hammond, M.A.	March 7th, 1901	,, ,,
Royle, Charles Leonard	November 7th, 1901.	December 5th.
Russell, James Bertram, B.Sc.	May 2nd, 1901	June 20th.
Ryffel, John Henry, B.A., B.Sc.	November 7th, 1901.	December 5th.
Sandford, Allan	June 20th, 1901	,, ,,
Sandford, Thomas	May 2nd, 1901	June 20th.
Scott, George Charlton	November 7th, 1901.	December 5th.
Scott, Herbert Kilburn	December 20th, 1900	February 7th.
Sheppard, Samuel Edward	May 2nd, 1901	June 20th.
Shepperson, William	February 21st, 1901	May 2nd.
Sherratt, C. Edmund Shaw	,, ,,	,, ,,
Sherwood, Edward Charles, M.A.	November 7th, 1901.	December 5th.
Sichel, Gerald T. S.	May 16th, 1901	June 20th.
Slefrig, Samuel, B.Sc.	March 21st, 1901	May 2nd.
Smith, Andrew Biggam	May 2nd, 1901	June 20th.
Smith, Henry Ewing	March 7th, 1901	May 2nd.
Smith, Harry Metcalfe	November 15th, 1900	February 7th.
Smith, James	March 21st, 1901	May 2nd.
Smith, Norman, B.Sc.	November 7th, 1901.	December 5th.
Spence, John Davidson	April 18th, 1901	June 20th.
Stell, Samuel Fenton	February 7th, 1901	May 2nd.
Stephenson, Robert, jun., B.A.	June 6th, 1901	December 5th.

Name.	Proposed.	Elected.
Talbot, John, B.A., B.Sc.	December 6th, 1900..	February 7th.
Tankard, Arnold Rowsby	May 16th, 1901	June 20th.
Tatam, George William G.	May 2nd, 1901	,, ,,
Taylor, William Henry	March 7th, 1901	May 2nd.
Templeman, William Henry	November 7th, 1901.	December 5th.
Thomas, Albert Edward, B.Sc.	December 20th, 1900	February 7th.
Tozer, Herbert Ackermann, B.A.	January 17th, 1901...	May 2nd.
Varley, Harold Foy F.	November 7th, 1901.	December 5th.
Verteuil, Joseph de	April 18th, 1901	May 2nd.
Wade, Frank	June 6th, 1901	December 5th.
Wager, Morton	,, ,, ...	,, ,,
Wallace, Herbert George	November 7th, 1901.	,, ,,
Waterhouse, J.	December 6th, 1900..	February 7th.
Wayland, William A.	,, ,,	,, ,,
Welch, George Edward, B.Sc.	February 7th, 1901...	May 2nd.
Whitehouse, Philip Lewington	November 7th, 1901.	December 5th.
Whittle, James	May 2nd, 1901	June 20th.
Whitton, William Arthur	April 18th, 1901.....	,, ,,
Wilson, Duncan R., B.A.	May 16th, 1901	,, ,,
Wilson, J. S., M.D., C.M.	December 6th, 1900..	February 7th.
Wylie, Adam Storer	February 7th, 1901..	May 2nd.

FELLOWS DECEASED.

Name.	Elected.	Died.
Beale, F. J.	May 4th, 1899.	May, 1901.
Beckett, John Hampden	May 4th, 1882	October 3rd, 1901.
Bird, Henry	June 4th, 1874	February, 1901.
Gilbert, Sir Joseph Henry	May 18th, 1841	December 23rd, 1901.
Hartridge, Alfred	December 1st, 1898	October 9th, 1901.
Hislop, Lawrence	April 21st, 1898	May, 1901.
Holliday, Robert	December 2nd, 1880	April 2nd, 1901.
Johnson, David	February 4th, 1875	December 17th, 1901.
Leonard, Norman	February 15th, 1894 ...	November 26th, 1901.
Macadam, Stevenson	February 21st, 1853	January 24th, 1901.
Madan, H. G.	May 1st, 1862	December 22nd, 1901.
Morris, G. Harris	February 19th, 1880	December 30th, 1901.
Shapleigh, Waldron	February 20th, 1873	September 24th, 1901.
Siebold, Louis	November 19th, 1874 ...	November 4th, 1901.
Spivey, W. T. N.	April 21st, 1898	October 25th, 1901.
Terrill, William	March 1st, 1877	July 24th, 1901.
Thomson, John	April 15th, 1858	September 3rd, 1901.
Thudichum, John L. W.	December 20th, 1860 ...	September 7th, 1901.

TITLES OF PAPERS COMMUNICATED TO THE SOCIETY DURING 1901.

	Page in Proceedings.	Page in Transactions.
January 17th.		
1. The preparation of iodic acid. By A. Scott and W. Arbuckle	2	302
2. Note on isomeric change and meta-substitution in benzenoid amines. By A. Lapworth	2	—
3. The preparation of esters from other esters of the same acid. By T. S. Patterson and C. Dickinson	4	280
4. Tecomin. A colouring matter derived from *Bignonia tecoma*. By T. H. Lee	4	284
5. A new method for the measurement of ionic velocities in aqueous solution. By B. D. Steele, B.Sc.	5	414
6. Metal-ammonia compounds in aqueous solution. Part II. The absorptive powers of dilute solutions of salts of the alkali metals. By H. M. Dawson and J. McCrae	5	493
7. The amide, anilide, and toluidides (ortho- and para-) of glyceric acid. By P. F. Frankland, F. M. Wharton, and H. Aston	6	266
February 7th.		
8. The action of hydrogen bromide on carbohydrates. By H. J. H. Fenton and Mildred Gostling	22	361
9. The ketonic constitution of cellulose. By C. F. Cross and E. J. Bevan	22	366
10. Note on a method for comparing the affinity values for acids. By H. J. H. Fenton and H. O. Jones	24	—
11. Organic derivatives of phosphoryl chloride and the space configuration of the valencies of phosphorus. By R. M. Caven, B.Sc.	26	—
12. αα-Hydroxycamphorcarboxylic acid. By A. Lapworth and E. M. Chapman	28	377
13. The bacterial decomposition of formic acid. By W. C. C. Pakes and W. H. Jollyman	29	386
14. Preparation of substituted amides from the corresponding sodamide. By A. W. Titherley, M.Sc., Ph.D.	29	391
15. Note on two molecular compounds of acetamide. By A. W. Titherley, M.Sc., Ph.D.	31	413
16. Diacetamide; a new method of preparation. By A. W. Titherley, M.Sc., Ph.D.	31	411

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17. Organic derivatives of silicon. By F. S. Kipping and L. L. Lloyd	32	449
18. Isomeric hydrindamine camphor-π-sulphonates. Racemisation of α-bromocamphor. By F. S. Kipping	32	370
19. Tetramethylene carbinol. By W. H. Perkin, jun.	33	329
February 21st.		
20. Isomeric hydrindamine mandelates and phenylchloroacethydrindamides. By F. S. Kipping and H. Hall.	36	442
21. Isomeric benzylhydrindamine bromocamphorsulphonates, and some salts of *d*-*l*-hydrindamine. By F. S. Kipping and H. Hall	37	430
22. Constitution of bromocamphoric anhydride and camphanic acid. By A. Lapworth and W. H. Lenton	37	1284
23. The action of acetylchloro- and acetylbromo-aminobenzenes on amines and phenylhydrazine. By F. D. Chattaway and K. J. P. Orton	38	461
24. The preparation of orthochloroaniline. By F. D. Chattaway and K. J. P. Orton	39	469
25. The bacterial oxidation of formates by nitrates. By W. C. C. Pakes and W. H. Jollyman	39	459
26. Condensation of phenols with esters of the acetylene series. Part IV. Benzo-γ-pyrone and its homologues. By S. Ruhemann and H. W. Bausor, B.A.	40	470
27. The influence of solvents on the rotation of optically active compounds. II. The influence of *iso*butyl alcohol and secondary octyl alcohol (methylhexylcarbinol) on the rotation of ethyl tartrate. By T. S. Patterson	40	477
28. Influence of a heterocyclic group on optical rotation; the ethyl and methyl salts of dipyromucyltartaric acid. By P. F. Frankland and F. W. Aston	41	511
March 7th.		
29. Nomenclature of the acid esters of unsymmetrical dicarboxylic acids. By J. J. Sudborough	43	—
30. Additive compounds of α- and β-naphthylamine with trinitrobenzene derivatives. By J. J. Sudborough	44	522
31. Acetylation of arylamines. By J. J. Sudborough	45	533
32. Formation of amides from aldehydes. By R. H. Pickard and W. Carter	45	520
33. A method of isolating maltose when mixed with glucose. By A. C. Hill, M.A.	45	—
34. The vapour pressure of aqueous ammonia solution. By E. P. Perman, D.Sc.	46	718
35. The influence of sodium sulphate on the vapour pressure of aqueous ammonia solution. By E. P. Perman, D.Sc.	47	725

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36. Formation of aromatic compounds from ethyl glutaconate and its derivatives. The reduction of trimesic acid and the conversion of tetrahydrotrimesic acid into tetrahydro*iso*phthalic acid. By W. T. Lawrence and W. H. Perkin, jun.	47	—
37. Optical activity of certain ethers and esters. By P. A. Guye	48	475
38. Halogen-substituted thiosinamines. By A. E. Dixon, M.D.	49	553
39. A form of tautomerism occurring amongst the thiocyanates of electro-negative radicles. By A. E. Dixon, M.D.	50	541
March 21st.		
40. Researches on morphine. Part II. By S. B. Schryver and F. H. Lees	54	563
41. The constitution of pilocarpine. Part II. By H. A. D. Jowett, D.Sc.	56	580
42. The chemical action of *Bacillus coli communis* and similar organisms on carbohydrates and allied compounds. By A. Harden	57	610
43. Action of dry silver oxide and ethyl iodide on benzoylacetic ester, deoxybenzoin, and benzyl cyanide. By G. D. Lander, D.Sc.	59	—
44. Alkylation of acylarylamines. By G. D. Lander, D.Sc.	59	690
45. The preparation of aliphatic imino-ethers from amides. By G. D. Lander, D.Sc.	61	701
46. Note on the latent heats of evaporation of liquids. By H. Crompton	61	—
47. On the atomic weight of lanthanum and on the error of the 'sulphate method' for the determination of the 'equivalent' of the rare earths. By Bohuslav Brauner and F. Pavlícek	63	—
48. On the atomic weight of praseodymium. By B. Brauner	65	—
49. On praseodymium tetroxide and peroxide. By B. Brauner	66	—
50. Note on neodymium. By B. Brauner	66	—
51. Contribution to the chemistry of thorium. By B. Brauner	67	—
52. Pheno-α-ketoheptamethylene and its derivatives. By F. S. Kipping and A. E. Hunter	68	602
53. Note on diphenyldinitroethylene. By J. J. Sudborough	68	—
54. Para- and ortho-cyanohydroxy-derivatives of pyridine. By J. Moir, M.A., B.Sc.	69	100*

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April 18th.		
55. Action of alkyl haloids on aldoximes and ketoximes. Part II. Alkylated oximes and isoximes and the constitution of aliphatic oximes. By W. R. Dunstan and E. Goulding	84	628
56. The supposed existence of two isomeric triethyloxamines. By W. R. Dunstan and E. Goulding	85	641
57. Nitrocamphene, aminocamphene, and hydroxycamphene. By M. O. Forster	85	644
58. A contribution to the chemistry of the triazoles. By G. Young and W. H. Oates	86	659
59. Researches on moorland waters. Part II. On the origin of the combined chlorine. By W. Ackroyd	87	673
60. Robinin, violaquercitrin, and osyritrin. By A. G. Perkin	87	—
61. Preparation of orthodimethoxybenzoin, and a new method of preparing salicylaldehyde methyl ether. By J. C. Irvine, B.Sc.	88	668
62. Action of hydroxylamine on the anhydrides of bromonitrocamphane. By M. O. Forster	88	653
63. On the estimation of cocaine and on di-iodo-cocaine hydriodide. By W. Garsed and J. N. Collie, F.R.S.	89	675
64. Note on acetonylacetone. By T. Gray	89	681
65. Condensation of acetonylacetone with hydrazine hydrate. By T. Gray	90	682
66. Preparation of synthetical glucosides. By H. Ryan, M.A., D.Sc., and W. S. Mills, M.A.	90	704
67. The influence of cane sugar on the conductivities of solutions of potassium chloride, hydrogen chloride, and potassium hydroxide; with evidence of salt formation in the last case. By C. J. Martin and O. Masson	91	707
68. The aluminium-mercury couple. Part III. Chlorination of aromatic hydrocarbons in presence of the couple. The constitution of the dichlorotoluenes. By J. B. Cohen and H. D. Dakin	91	1111
69. A modification of Gutzeit's test for arsenic. By E. Dowzard	92	715
70. On the chemistry of *Nerium odorum*. By R. C. L. Bose, M.B.	92	—
71. Change and interaction in organic compounds. By A. Lapworth	93	1265
72. The mechanism of the Claisen reaction. By A. Lapworth	95	—
73. A new series of di-mercuri-ammonium salts. Part I. By P. C. Ray, D.Sc.	96	—
May 2nd.		
74. The synthetical formation of bridged-rings. Part I. Some derivatives of bicyclopentane. By W. H. Perkin, jun., and J. F. Thorpe	110	729

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75. Lead silicates in relation to pottery manufacture. By T. E. Thorpe, C.B., F.R.S., and C. Simmonds, B.Sc.	113	791
76. The preparation and properties of 2:6-dibromo-4-nitrosophenol. By M. O. Forster and W. Robertson	116	686
77. The chlorination of toluene. By W. P. Wynne	116	—
May 16th.		
78. Derivatives of methylfurfural. By H. J. H. Fenton and Miss M. Gostling	119	807
79. Optically active nitrogen compounds and their bearing on the valency of nitrogen; dextro- and lævo-α-benzylphenylallylmethylammonium salts. By W. J. Pope and A. W. Harvey	120	828
80. Reactions of hydroxyoxamides. By R. H. Pickard and W. Carter	123	841
81. The *sym*-trichlorobromoanilines; and chloro- and bromo-amino-derivatives of chlorobromoacetanilides. By F. D. Chattaway and K. J. P. Orton	124	816
82. Replacement of bromine by chlorine in anilines. By F. D. Chattaway and K. J. P. Orton	125	822
83. The absorption spectra of cyanogen compounds. By W. N. Hartley, F.R.S., J. J. Dobbie, D.Sc., M.A., and A. Lauder, B.Sc.	125	848
84. The nutrition of yeast. Part III. By A. L. Stern, D.Sc.	126	943
85. On the colloid form of piperine, with especial reference to its optical refraction and dispersion. By H. G. Madan	127	922
86. Note on pyromucylhydroxamic acid. By R. H. Pickard and A. Neville	127	847
87. The condensation of ethyl phenyl ketone with benzaldehyde. By R. D. Abell, B.Sc.	128	928
88. A new method for the determination of hydrolytic dissociation. By R. C. Farmer, B.Sc., Ph.D.	129	863
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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

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January 17th, 1901. Professor THORPE, C.B., F.R.S., President, in the Chair.

Messrs. E. F. Hudson, H. A. Auden, and A. H. Mitchell were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Percival James Burgess, Singapore; Raymond Dubois, Rutherglen, Victoria; Oscar Loewenthal, Mill Hill Park, London, W.; Walter Stevens Crocker, 25, Upper Parliament Street, Liverpool; Herbert Ackerman Tozer, 113, Stepney Green, London, E..

The following letter has been sent, at the direction of the Council, to Professor Markownikoff of the University of Moscow, a Foreign Member of the Society, on the occasion of the commemoration of the 40th year of his Doctorate.

DEAR SIR,

At the last meeting of the Council of the Chemical Society I had the pleasure of submitting your letter of December 8th, concerning the proposed celebration in honour of Prof. Dr. Wladimir Markownikoff. I am instructed by the Council to inform you that it will not be possible for any of our Fellows to be present personally on February 25th, but I am to ask you to be so good as to convey to Prof. Markownikoff the hearty congratulations of our Society, and to express the wish that he may be spared to carry on his valuable and important investigations for many more years. We

rejoice that your distinguished countryman's name appears in our list of Foreign Members, and I beg you to convey to him the assurance that his long devotion to that science which he has done so much to advance by his researches is most highly appreciated by English chemists.

Yours obediently,

RAPHAEL MELDOLA,

Foreign Secretary.

DR. H. DECKER.

Of the following papers, those marked * were read :—

***1. "The preparation of iodic acid." By A. Scott and W. Arbuckle.**

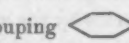
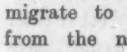
The usual method of preparing iodic acid by gently boiling iodine with nitric acid in a flask with a long neck, is tedious when any quantity is required and liable to great loss of iodine unless the source of heat is very carefully regulated. By using, first the ordinary form, and later a modified form, of Soxhlet's fat extraction apparatus to contain the iodine, almost theoretical yields of iodic acid were obtained after a very short treatment with the boiling nitric acid. The liability, however, of the siphon tube to become choked with crystals of iodic acid led to the abandonment of this type of apparatus. After many trials with various forms of apparatus, the authors recommend the use of a round-bottomed flask having a ground-in neck carrying two tubes, to one of which is sealed a reflux condenser, and through the other is fitted a tube by means of which a current of oxygen is passed through the boiling liquid. With this apparatus *finely powdered* iodine boiled with ten times its weight of fuming nitric acid may be completely oxidised in 20—30 minutes.

***2. "Note on isomeric change and meta-substitution in benzenoid amines." By A. Lapworth.**

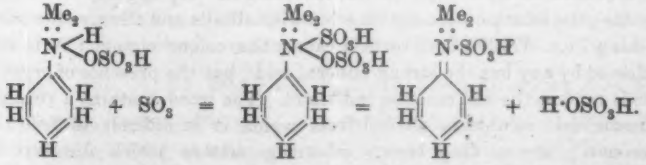
The rules deduced from the two simplest change forms (*Trans.*, 1898, 73, 457) depend on the assumption made implicitly throughout the paper, that only one group can "migrate" along any chain of atoms at any instant, that is, that exchange of groups is, as a rule, the result of the successive migration of the two groups in reverse directions. This view appears in general to be well founded, and it is easily demonstrated that if it holds true, the rules deduced are necessarily correct, the second being used where the valency of an atom alters. It is of no consequence whatever how the migration is effected, so far as the applicability of the rules is concerned.

Although in applying the rules it is sometimes convenient to assign successive positions of attachment of a labile group in its migration, it is not imagined that these are actually occupied, at least in the ordinary sense of the term. It may be supposed, for example, that the group is handed on in a still dissociated state from its initial to its final position, the others merely representing the possible places of attachment.

The author has advanced the view that *meta*-substitution is the result of elimination of a hydrogen atom in the benzenoid nucleus (necessarily from the *meta*-position) with a group in the complex formed by union of the side chain with the acting agent. Armstrong has recently used a similar conception in explaining the formation of chloracetanilides from phenylacetylchloramines; in the author's opinion, this would lead to the production of the *meta*-derivative, instead of, as is the case, the *ortho*- and *para*-derivatives (compare *Trans.*, 1900, **77**, 1051).

In alluding to the formation of *meta*-sulphonic acids from benzenoid amines (*loc. cit.*, p. 457), the author suggested that it was the result of the migration of the $-SO_3H$ group in aniline sulphates; this view must be rejected as impossible, as the necessary grouping is not present. The statement that *meta*-derivatives are formed when the labile group M is separated from the benzene ring by two atoms only holds true when the grouping  is present or can be formed as an intermediate step. M will migrate to the *meta*-position when separated by one atom only, from the nucleus if the intermediate compound is of the type  , and X is able to fall in valency by two units, for example, when X is a pentavalent nitrogen atom.

Applying this to the case of the action of fuming sulphuric acid on dimethylaniline, the most probable explanation of the reaction is that dimethylaniline sulphate unites with sulphuric anhydride, and that from this compound sulphuric acid is then eliminated by loss of a hydrogen atom from the nucleus thus



The latter substance must yield the meta-sulphonic acid if the sulpho-group then migrates, assuming, as usual, that the other atoms

retain their positions until this migration has ended. Or, expressing it in terms of the author's rules, as the sulpho-group migrates the valency of the nitrogen must fall, since it cannot become attached to the nucleus by a treble binding; the nearest possible position of attachment for the labile group is, therefore, the β-position, hence, as the valencies of the carbon atoms remain constant, the next position must be imagined to be reached by an $\alpha\gamma$-change. This process can also be followed by using Thiele's rule, but, in this case, it must be assumed that sulphuric acid is added in one way and eliminated in another, and as for this purpose it must be supposed that before addition it breaks up into HO and $\cdot SO_3H$ instead of into H and OSO_3H, the objection to this hypothesis is obvious.

3. "The preparation of esters from other esters of the same acid." By T. S. Patterson and C. Dickinson.

Experiments were described which had for their object the preparation of methyl ethyl tartrate. A substance was obtained having the observed rotation $+11{\cdot}14°$ at $18°$ ($l = 200$ mm.), which probably consisted chiefly of the compound sought. It showed no tendency to crystallise and as no method of purification, other than crystallisation, was likely to be suitable, these attempts to obtain a pure compound were abandoned. They had shown, however, that ethyl tartrate is largely converted into methyl tartrate by the action of methyl alcohol and hydrochloric acid. Experiments were then described showing that pure ethyl tartrate can be obtained from methyl tartrate and pure methyl tartrate from ethyl tartrate, by Fischer's method, hence it is probable that any other ester may be prepared by an analogous process, under certain circumstances this might prove useful.

Finally determinations of the rotation of methyl tartrate at temperatures between 20° and 100° were given.

4. "Tecomin. A colouring matter derived from 'Bignonia tecoma'." By T. H. Lee.

The new colouring matter is a yellow, crystalline, substance soluble in alcohol with an orange colour, insoluble or very slightly soluble in water; the solution becomes rose-red with alkalis and clear yellow with acids; 2 c.c. $N/100$ alkali or acid causes the colour change; it is not affected by any but the strong mineral acids, but the presence of organic acids renders the end reaction indistinct. The wood contains a reddish-brown resin soluble in alcohol from which it is difficult to free the tecomin; also a deep brown colouring matter which dissolves in aqueous alkalis and is precipitated by acids. It is used locally as a dye for cotton and as a stain for wood.

5. "A new method for the measurement of ionic velocities in aqueous solution." By B. D. Steele, B.Sc.

The author described a new method for the direct measurement of ionic velocities in aqueous solution. Masson (*Phil. Trans.*, 1899, **192**, A, 331) has succeeded in obtaining satisfactory measurements in gelatine, and for a few ions; Whetham (*Phil. Trans.*, 1893, **184**, A, 337) has made measurements in water. The method now described should be a perfectly general one, as the use of coloured indicator solutions is no longer necessary, and hence the range of ions which may be used as indicators is largely increased.

The method consists in enclosing the liquid to be measured between two partitions of gelatine, which contains the indicator ion in solution; on the passage of the current the cation of the solution is followed by the cation of the indicator, and the anion of the solution by the corresponding anion of the indicator. It is necessary in all cases that these indicator ions should move more slowly than the measured ion.

The position of the boundary between the two solutions is easily seen, on account of the difference in refraction, and the motion is measured by means of a cathetometer. If the above-mentioned condition is fulfilled the relative velocity of the boundary is not influenced by changing the indicators, thus ($CuSO_4$ and K_2CrO_4), ($CuSO_4$ and $NaC_2H_3O_2$), and ($CdSO_4$ and $NaC_2H_3O_2$) all gave the same value for the transport number of $MgSO_4$.

The absolute velocity of a few ions has also been calculated and compared with the velocities found by Kohlrausch, and a very fair agreement is shown to exist between the two sets of measurements.

6. "Metal-ammonia compounds in aqueous solution. Part II. The absorptive powers of dilute solutions of salts of the alkali metals." By H. M. Dawson and J. McCrae.

The influence exerted by the addition of salts of the alkali metals on the distribution of ammonia between water and chloroform at 20° has been investigated. It has been found that so long as the ammonia concentration in the aqueous phase is less than 0·5 normal, the alteration of the distribution coefficient is proportional to the salt concentration, that is, the expression $\frac{k-k'}{n}$ is constant, where k is the distribution coefficient with pure water (26·28), and k' is the observed distribution coefficient with salt solution of normality n. This constant it is proposed to call the "equivalent alteration of the distribution coefficient."

The alteration for each salt is composed additively of two values, one dependent upon the cation, the other upon the anion. Since, according to the views of Abegg and Bodländer, "ammonia-complex" formation takes place only with the cation, the differences in the values of the alteration for salts of one metal express the differences in the physical actions of the anions; but differences in the values for salts containing the same anion do not measure the differences in the physical actions of the cations because of the complicating influence of complex formation. The lithium salts show the greatest tendency to form ammonia addition compounds, ammonium salts show it to a less degree, whilst for sodium salts it is probably very small, but greater than for potassium salts.

When the ammonia concentration is greater than 0·5 normal, irregularities occur, and it has been found that for increasing salt concentration and constant ammonia concentration the value of $\frac{k-k'}{n}$ decreases, whilst for constant salt concentration and increasing ammonia concentration it increases.

Non-electrolytes (urea and cane sugar) also considerably affect the distribution coefficient, so that Dalton's law is not obeyed.

These results indicate that the solvent power of water is changed to a varying extent by the different ions. The intrinsic property of the ion which is the cause of this difference is not deducible from the ionic theory as it stands at present.

7. "The amide, anilide, and toluidides (ortho- and para-) of glyceric acid." By P. F. Frankland, F. M. Wharton, and H. Aston.

These compounds have been prepared by the authors with the object of investigating the influence on the rotation produced by replacing the alkoxyl group by the amido-group and its substituted derivatives. After a review of the limited number of cases at present available for ascertaining these relations, the authors pointed out that so far it was observable that if in an homologous series of ethereal salts the rotation is raised by successive additions of CH_2, then the amide has a similar but still higher rotation than the ethereal salts, but that if the successive additions of CH_2 lead to diminished rotation, then the corresponding amide has a lower rotation than the ethereal salts. The first of these relations is exhibited by the derivatives of tartaric, malic, and glyceric acids, whilst the only hitherto known example of the second is furnished by the corresponding derivatives of mandelic acid.

The result of substituting in the amido-group appears in all cases to be an increase in the rotatory effect of the latter. In the case of

malic acid, the anilide has a greater molecular rotation than the amide, the *o*-toluidide greater still, and the *p*-toluidide the greatest of all. In the case of glyceric acid, on the other hand, although the anilide has a greater molecular rotation than the amide, the rotation of the *p*-toluidide is less than that of the anilide, and the rotation of the *o*-toluidide is about the same as that of the amide.

The amido-compounds prepared by the authors appear to be the only ones which have hitherto had their rotation determined in the liquid state; in the case of the *o*-toluidide, however, this could unfortunately not be effected, as this, on fusion, at once acquired a strong colour. In consequence of this, the rotation of all the compounds in question was determined also in methyl alcohol solution.

The corresponding compounds of inactive glyceric acid were also prepared, and their melting points compared with those of the active substances.

ANNIVERSARY DINNER.

It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Wednesday, March 27th, 1901, the day preceding that fixed for the Annual General Meeting. Further particulars will shortly be announced.

At the next meeting, on February 7th, there will be a ballot for the election of Fellows, and the following papers will be communicated :—

"The action of hydrogen bromide on carbohydrates." By H. J. H. Fenton and Mildred Gostling.

"Note on a method of comparing the affinity-values of acids." By H. J. H Fenton and H. O. Jones.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

The following Candidates have been proposed for election. A ballot will be held on Thursday, February 7th, 1901.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Aitken, Andrew Charles,
Rio Marina, Isola d'Elba, Italy.

Analytical Chemist. Six years assistant to Messrs. Tatlock and Thomson, Analytical Chemists, Glasgow. Two years sole Chemist with the White Lead Company, Limited, Glasgow. For the last two years representative in Elba for Messrs. H. Borner and Co., Limited, London.

R. R. Tatlock. Horatio Ballantyne.
R. T. Thomson. Robt. D. Connell.
James E. Ferguson.

Barrie, Thomas Stewart,
77, Sinclair Drive, Langside.

Principal of the West of Scotland College of Pharmacy, 157, St. Vincent Street, Glasgow. Student of Chemistry at Grove Street Public School 1891—1893, Technical College 1893—1894, both in Glasgow; also in Crumphill Public School, Paisley, 1894—1895; gained the Minor Qualification (Oct., 1896) and the Major Diploma (Jan., 1898) of the Pharmaceutical Society of Great Britain; elected a Member of that body, 1900. Teacher of Chemistry at the West of Scotland College of Pharmacy, Glasgow, and Consulting Chemist there. Author of a book on "Volumetric Analysis" adapted for pharmaceutical students, and contributor of various articles dealing with the analysis of arsenates, lactophosphates, calamine, iodides, &c., to the *Pharmaceutical Journal* and the *Chemist and Druggist* during the years 1899 and 1900.

G. G. Henderson. Thos. Maben.
James Robson. *Thomas Gray.*
Matthew A. Parker.

Bedwell, John Cardew, B.Sc. (London),
65, High St., Colchester.

Private Tutor and Science Teacher. For 3 years Assistant Lecturer on Chemistry at Colchester Technical College. Student at Technical Laboratory, Chelmsford 1 year, and at Colchester Technical College 3 years. Desirous to obtain Society's Journal for assistance in research.

Thos. S. Dymond. William Briggs.
Frank Hughes. *W. A. Shenstone.*
J. W. Shepherd.

Bult, Herbert John,
165, Brixton Hill, S.W.

Chemist. Three years student at Finsbury Technical College. Two years in laboratory at St. George's Hospital, last 18 months as Chief Assistant. For some time in charge of laboratory of Messrs. Thomas Farmer and Co., Silvertown. Two years Chief Assistant to Dr. P. Dvorkovitz, Petroleum expert. One year Head Chemist and Assistant Engineer at European Petroleum Co.'s Thames Haven Refinery. Some time chemist to Mr. A. Adiassewich, Petroleum expert. Three years private practice.

R. Meldola. Lawrence Briant.
Boverton Redwood. F. Southerden.
Arthur J. Starey.

Burrows, Merrick William,
Dunkirk, Devizes; 4, St. George's Terrace, Wilton, Taunton.

Science Master (Huish School, Taunton). For three years, 1891—1894, student in Owens College Chemical Department. B.Sc. Vict., Hons. Chemistry, 1894. M.Sc. 1898. Assisted Prof. Dixon in research on the action of carbonic acid on heated carbon 1894—1895.

H. B. Dixon. G. H. Bailey.
W. H. Perkin, jun. William A. Bone.
D. L. Chapman.

Cohen, Robert Waley,
11, Hyde Park Terrace, London, W.

B.A. Cambridge. Has long been interested in Chemistry, and proposes to devote himself to some branch of Industrial Chemistry. Made Chemistry an important subject at Cambridge, and desires to join the Society in order to continue and extend his knowledge of the subject by means of its meetings and publications.

W. A. Shenstone. H. J. H. Fenton.
H. E. Roscoe. W. T. N. Spivey.
C. T. Heycock.

Cousins, Herbert Henry,

Government Laboratories, Kingston, Jamaica.

Government Analyst and Agricultural Chemist. First Class Hon. Chemistry, Oxford. M.A. Eighteen months in laboratory of V. Meyer, Heidelberg. Assistant Demonstrator to Waynflete Professor, Oxford. Lecturer on Chemistry, University Extension. Lecturer on Chemistry at S.E. Agricultural College, Wye. Now Chemist for Jamaica. Paper with J. E. Marsh in *Trans.*, 1891. "Farm Foods," 1895. "Chem. of Garden," 1898. Researches on hop analysis, insecticides, manuring of crops, &c.

John Percival. W. W. Fisher.
A. D. Hall. V. H. Veley.
J. E. Marsh.

Daniel, Gilbert Howard,

21, Church Walk, Ulverston.

Head Master, Higher Grade and Technical Schools, Ulverston. B.Sc. (Lond.), 1890. Registered Teacher (South Kensington) in Prac. and Theor. Org. Chem. and in Prac. and Theor. Inorg. Chem. Head Master of Maryport Higher Grade School and Chemistry Lecturer in the Evening Classes also, 1891–97. Head Master of Bristol North Street Higher Grade School and Evening Class Lecturer, 1897–1900.

J. H. Haynes. R. S. Cahill.
R. L. Taylor. *F. W. Wormell.*
James Foulds.

Dodd, Robert,

28, Sibella Road, Clapham, S.W.

Student at King's College. Now Chemist in Boracic Acid Works. One year at the "Allan Glen's School," Glasgow. Three years St. Clement Danes Schools. Student in the Chemical Department King's College, London, during 1896—1897, 1897—1898.

John M. Thomson. *Oscar Gutmann.*
Herbert Jackson. *B. E. R. Newlands.*
Patrick H. Kirkaldy. *Arthur R. Ling.*
Thos. A. Cheetham. *Rudolph Messel.*

Donnan, Frederick George, M.A., Ph.D.,

Chemical Laboratory, University College, Gower Street, W.

Assistant, Chemical Department, University College, Gower Street, W. Author of following papers: "An Attempt to give a simple Theoretical Explanation of Raoult's Law," *Phil. Mag.*, Nov., 1892, 411; "Electrolytic Dissociation and Light-Absorption in Solutions," *Zeitschr. Phys. Ch.*, 19, 465; "The Saturation-Pressures of the

System, $Mg{\cdot}K{\cdot}Cl{\cdot}SO_4$," *Sitz. Ber. Akad.*, 52, 1897; "Theory of the Thomson-Effect in a Binary Electrolyte," *Phil. Mag.*, June, 1898, 529; "Theory of the Hall-Effect in a Binary Electrolyte," *Phil. Mag.*, Nov., 1898, 465; "The Isothermal Pressure-Surface for one Double and two Single Salts," *Journ. Phys. Ch.*, 2, 417; "The Nature of Soap Emulsions," *Zeitschr. Phys. Ch.*, 31, 42; "Relative Rates of Effusion of Helium, Argon, and some other Gases," *Phil. Mag.*, May, 1900, 423.

William Ramsay. Edward C. Cyril Baly.
Morris W. Travers. Alex. M. Kellas.
Vaughan Harley. J. Nevill Huntly.

Emery, John Alfred,

Cinderford, Gloucestershire.

Head Master. Higher Grade Bd. Schools, Cinderford, Glos. Superintendent Teacher of Physics and Chemistry in above schools. Holder of Certificates in above subjects under Science and Art Dept., South Kensington. Teacher of Pupil Teachers' Classes in Chemistry, &c.

J. Jackson. *Sydney Young.*
Thomas Edwards. *F. Wallis Stoddart.*
Thos. W. Berry. *Austin Keen.*

Ferguson, Reginald Williams, A.R.C.S.,

8, Havelock Terrace, Paisley Road, Glasgow.

Senior Assistant in the Chemical Department of the Leeds Institute of Science, Art and Literature. National Scholar in Chemistry and Physics; Associate (in Chemistry) of the Royal College of Science, London. "Stenhouse Scholar" and Associate of the Glasgow Technical College. For 6 years a Student of Chemistry under, successively, Prof. Dittmar, Prof. Thorpe, and Prof. Tilden. Since 1895 engaged in lecturing on Chemistry in the schools of the Leeds Institute, and in the management of a large Chemical Laboratory.

T. E. Thorpe. W. Palmer Wynne.
William A. Tilden. George Ward.
Thomas Fairley.

Houldershaw, Arthur,

71, Lavender Gardens, West Jesmond, Newcastle-on-Tyne.

Science Instructor in Chemistry, Physiology, and Hygiene in Elementary School. Studied Inorganic and Organic Chemistry for many years, and secured several Certificates in same at South Kensington Exams. 1st Class Certificates in advanced Physiology (Queen's Prize, 1892, one of five), and Hygiene, and Teacher of these subjects for some years under Science and Art Department. Reasons: To become better acquainted with recent researches in Chemistry

by means of the Journal of the Society, and to participate in the privileges granted to Fellows.

T. W. Lockwood. *Joseph Brown.*
I. Patchett. *R. S. Cahill.*
Frank R. Dudderidge. *Oliver Kirk.*
W. Goddard.

Howard, Bernard Farmborough,
Devon House, Buckhurst Hill, Essex.

Chemical Student at the City and Guilds of London Institute, Technical College, Finsbury. Educated at Marlborough College, 1894—1898. Since then Chemical Student under Professor Meldola, F.R.S., F.I.C., F.C.S., at Technical College, Finsbury.

R. Meldola. F. Southerden.
David Howard. D. Lloyd Howard.
Alfred G. Howard.

Hughes, Edward,
Rectory, Barmouth.

Clerk in Holy Orders. I am much interested in Chemistry, practical and theoretical, and desire to avail myself of the publications of the Society. I was a pupil of Prof. Vacher, Editor of *Fresenius Quant. and Qual. Analyses.*

Watson Smith. Thomas Wardle.
R. Le Neve Foster. *W. F. Keating Stock.*
Alex. K. Miller.

Hutton, Robert Salmon, M.Sc.,
Owens College, Manchester.

Demonstrator in Electrochemistry. Student for 4 years in Chemical Laboratories, Owens College. B.Sc. Hons. Chem., 1897. Has investigated the "Compound Line Spectrum of Hydrogen" given by specially purified hydrogen (*Phil. Mag.*, Sept., 1898). Has studied physical chemistry for 2 years in Leipzig under Prof. Ostwald, and in Paris under Prof. Moissan.

H. B. Dixon. G. H. Bailey.
W. H. Perkin, jun. E. J. Russell.
William A. Bone. D. L. Chapman.

Ionides, Stephen Archigenes,
Balliol College, Oxford.

Student of Chemistry at Balliol College, Oxford.

D. H. Nagel. A. F. Walden.
H. B. Hartley. P. Elford.
H. L. Bowman.

Jones, John Lloyd Thomas Major, I.M.S.,
United Service Club, Calcutta.

Deputy Assay Master, Calcutta, and lately for 1½ years Acting Assay Master, Calcutta. Bachelor of Medicine, University of Durham. Member of the Royal College of Surgeons, England. Diplomate of Public Health, Cambridge University. Passed the Course of Instruction in Assaying at the Royal College of Science, South Kensington, and Royal Mint, London.

W. C. Roberts-Austen. Chapman Jones.
F. W. Bayly. T. E. Thorpe.
T. K. Rose. W. J. Russell.

Jones, Robert Henry,
Glen Albyn, Coity Road, Bridgend, Glam.

Science Master, County School, Bridgend, Glam. B.Sc. (Vic.). 1st Class Hon. in Chem. 1896. Research Student with Prof. Dixon 1896—8. Dalton Chemical Scholar of Owens College, 1897. Original work: "Instantaneous pressure produced on Collision of two Explosion Waves," Manch. Lit. and Phil. Soc. M.Sc. (Vic.), 1899. 1898—9 Science Master, Wellington Coll., Salop; 1899, Science Master, County Sch., Bridgend.

H. B. Dixon. W. H. Perkin, jun.
W. A. Bone. E. J. Russell.

H. C. H. Carpenter.

van der Linde, Harold Theodor Granville,
101, Tyndall Avenue, Toronto, Canada.

Chief Chemist, Gutta Percha and Rubber Manufacturing Co. of Toronto. Above position (with average of four assistants) for past seven years, previous to which I was Manager (with charge of chemical laboratory) to the Edison General Electric Co. (manufacturing every description of electric appliance and insulated conductor) in Canada, for four years. At Edinburgh University passed in first B.Sc. and first and second M.B., C.M. Exams.

Alex. Crum Brown. Charles G. Cresswell.
W. H. Ellis. *G. G. Henderson.*

David Howard.

Martin, Nicholas Henry,
Ravenswood, Low Fell, Gateshead, and Royal Societies Club, London.

Pharmaceutical Chemist. Manufacturer of pure chemicals. Chairman of the Newcastle Section of the Society of Chemical Industry.

P. Phillips Bedson. Wyndham R. Dunstan.
Alexander Scott. F. C. Garrett.

S. Hoare Collins.

Menzies, James,

39, Winterbrook Road, Herne Hill, London, S.E.

Chemical Engineer. Studied chemistry and passed examinations at Clausthal Mining College, Germany, afterwards in the Berlin "Polytechnik." Was 2½ years with D. A. Sutherland, Esq., F.C.S., F.I.C., as Assistant. At present with J. C. Butterfield, Esq., F.I.C., F.C.S., M.I.M.M., M.R.I.

D. A. Sutherland. — Robert N. Lennox.
James Mactear. — J. C. Butterfield.

Thomas Fairley.

Moir, James, M.A., B.Sc.,

The Ash, 62, Hamilton Place, Aberdeen, Scotland.

1851 Exhibition Scholar, Aberdeen University. Joint author with Dr. Japp of paper on "Constitution of Amarine, its so-called Dialkyl- and Diacyl-derivatives, and of Isoamarine" (*J. C. S.*, May, 1900). Lately Junior Assistant, Chemical Department, Aberdeen University. At present Research Student at Central Technical Inst., South Kensington.

Henry E. Armstrong. — Gerald T. Moody.
F. R. Japp. — W. A. Davis.

T. Martin Lowry.

Meredith, William,

63, Albion Place, Ulverston.

Lecturer for 15 years in Chemistry and Physics. Superintendent of Evening Continuation School. At Ulverston I have no means of access to the Society's Journal, and I should find it of real interest and benefit to me in my work.

Wm. Cranfield. — G. S. Turpin.
A. E. Tutton. — *Chapman Jones.*

James C. Philip.

Nunn, Arthur W.,

313, Sydenham Road, Sydenham, S.E.

Analytical Chemist. Has been for 12 years and is now engaged in analytical work, chiefly foods and drugs. Has contributed several papers on Pharmaceutical Chemistry, *e.g.* "On a supposed change in Calomel when kept in contact with Sugar for a long time." Has passed the Major Examination of the Pharmaceutical Society. Has delivered public lectures in his parish.

John Attfield. — C. A. Hill.
W. Watson Will. — W. Chas. Sayers.

H. A. D. Jowett.

Page, Theodore Henry,
40, Wilson Road, Camberwell, S.E.

At present employed in Research Laboratories of London Essence Co., George Street, Camberwell. Associate of City and Guilds of London Institute (Chem. Dept.).

Henry E. Armstrong. T. M. Lowry.
William J. Pope. Edwin C. Jee.
Gerald T. Moody. William A. Lethbridge.

Price, Thomas Slater,
University College, Sheffield.

Demonstrator in Chemistry. "The Amyl (Secondary Butyl Methyl) derivatives of Glyceric, Diacetylglyceric and Dibenzoylglyceric acids, active and inactive" (*Journ. Chem. Soc.*, 1897, p. 253) (in conjunction with Prof. Frankland.). "Die Reaktion zwischen Kaliumpersulphat und Iodkalium, und Katalyse bei derselben," *Zeit. f. Phys. Chemie*, 27, 474; "On the Temperature Coefficient of Ester saponification," *Swedish Academy*, 1900; "The Reaction between Ethyl Alcohol and Hydrochloric Acid," *Proceedings Chem. Soc.*, Nov., 1900. 1851 Exhibition Scholar in Chemistry, 1896—1899. Ph.D. (Leipzig), 1898. D.Sc. (Lond.), 1900. A.I.C., Jan., 1900.

W. Carleton Williams. Henry J. S. Sand.
Percy F. Frankland. George Young.
W. R. Innes.

Radcliffe, Lionel Guy,
6, Alma Terrace, Old Trafford, Manchester.

Lecturer in Chemistry. Lectures on Organic and Inorganic Chemistry, at the Municipal Technical School, Manchester; also had experience in Technical Chemistry in Colour Works. Has also published original work on the following subjects: On "Curcumine" (*Journal of Society of Dyers and Colourists*); on "Carthamine" (*ibid.*); "The Oximes of Indigotin and Indirubin, &c." (*ibid.*); together with Dr. L. Marchlewski, "Zur Kenntniss des Indigotins" (*Journal für praktische Chemie*) and in (*Ber. d. deutschen Chem. Ges.*) "Note on the constitution of Indican, &c." (*Journal Soc. of Chem. Industry*), &c.

W. H. Perkin, jun. John Allan.
Edw. Schunck. Jas. Grant.
Jul. Hübner.

Ramsden, William Cecil,
13, Effra Road, Rathmines, Dublin.

Junior Assistant and Demonstrator. I was a student in the Chem. Dept. of Univ. Coll. Nottingham, for over 3 years, then acted

as Lecture Assist. to Prof. Snape, U.C.W., Aberystwyth, for 3 years, and am now Junior Assistant and Demonstrator to Prof. J. E. Reynolds, T.C., Dublin, with whom I was associated in some work on the electrolytic estimation of bismuth. This work has been published in a short article.

J. Emerson Reynolds. Frank Clowes.
Emil A. Werner. J. Bernard Coleman.
Edward T. Shelbourn.

Scott, Herbert Kilburn,
P.O.B. 634, Rio de Janeiro, Brazil.

Mining Engineer, Metallurgist, and Analytical Chemist (consulting). Was with Dr. E. Riley, City Road, London, in 1892. Later Chemist Elba Iron Mines, afterwards, 1895, Chief Engineer and Manager. Manager, Manganese Mines, Brazil, 1895—1900. Now established in Rio de Janeiro as above. Author of "Iron Mines of Elba," 1895, "Manganese Ores of Brazil," 1900 (*Proc. Iron and Steel Institute*).

Edwd. Riley. B. A. Burrell.
Archie H. Strong. Robt. D. Connell.
James E. Ferguson.

Smith, Harry Metcalfe,
79, Helix Road, Brixton, London, S.W.

Analytical Chemist. Fellow of the Institute of Chemistry. Member of the Society of Public Analysts. Now, and for 10 years past, Assistant to Dr. Thos. Stevenson, Guy's Hospital. Joint author with Norman Leonard, B.Sc., of a number of papers on analytical subjects contributed to *The Analyst*.

Thos. Stevenson. Charles E. Groves.
William Ramsay. J. Norman Collie.
Norman Leonard.

Talbot, John,
Tunstall House, Harrow.

Assistant Science Master at Harrow School. Late Scholar of Trinity College, Cambridge. B.A. (Camb.), 1st Class, parts I and II, Nat. Science Tripos. B.Sc. (Lond.), Exhibitioner in Chemistry and Physics, and Medal in Physics at Intermed. B.Sc. First Class Honours Physics, Final B.Sc.

M. M. Pattison Muir. T. B. Wood.
S. Ruhemann. W. T. N. Spivey.
R. S. Morrell. B. P. Lascelles.

Thomas, Albert Edward, B.Sc. (Lond.), A.I.C.,
34, South Road, Kingswood, Bristol.

Assistant Lecturer on Chemistry and Physics, Merchant Venturers' Tech. Coll., Bristol. B.Sc. (Lond.), with Honours in Chemistry and Physics. A.I.C. by examination. First Class Honours in Theor. and Pract. Inorganic Chemistry, &c. (South Kensington). 5½ years' teaching experience as above.

J. Wertheimer. Arnold Philip.
G. P. Darnell-Smith. Ernest H. Cook.
Sydney Young.

Waterhouse, James,
Oak Lodge, Court Road, Eltham, Kent.

Major-General, Indian Staff Corps. Late Assistant Surveyor-General of India, in charge Photographic and Lithographic Office, S.I.D., Calcutta. Has published original researches on the action of eosin and other dyes on photographic plates; on the action of thiocarbamides in reversing the photographic image on gelatine dry plates; and on the sensitiveness of silver to light.

R. Meldola. John Spiller.
Chapman Jones. Charles H. Bothamley.
J. W. Swan.

Wayland, William A.,
4, Harefield Road, Brockley, S.E.

Manufacturing and Analytical Chemist. A manufacturer of chemicals, also analyst, specialising water, malt, hops, &c. Interested in chemistry in its relation to the brewing and sugar industries.

William J. Pope. Herbert F. Fermor.
Stanley J. Peachey. Alfred W. Harvey.
Arthur H. Coote.

Wilson, James Scott,
Bradford St., Walsall.

Medical Officer of Health. M.D., C.M. Glas. Univ. D.P.H. Camb. For twelve months a student in the Laby. of Dr. B. Hill, Birmingham, and at present engaged in chemical work in connection with Public Health.

Alfred Hill. James Robt. Kaye.
Chas. A. MacMunn. *Frank Clowes.*
J. B. Coleman.

The following Certificate was authorised by Council under Bye-Law I (3):—

Haddon, Henry Edward,
Pamplemousses, Mauritius.

Chemist of the "Beau Plan" Sugar Estates Company, Limited. Analytical Chemist of the Faculté de Medicine et Pharmacie de Lyon. Ex-Chemist of the "Sucrerie Centrale" de Meaux, Seine et Marne, France. Ex-Chemist of the "Las Angustias" factory, Granada, Spain. Member of the Chemical Society of Paris. Member of the Association des Chimistes de Sucreries, France. Author of several papers on cafetannic acid and milk. Ex-Ag. Assistant Director of the "Station Agronomique" of Mauritius.

Vivian B. Lewes.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 232.

February 7th, 1901. Professor THORPE, C.B., F.R.S., President, in the Chair.

Messrs. R. M. Caven and J. B. Harrison were formally admitted Fellows of the Society.

The following certificates were read for the first time:—William Carrick Anderson, 2, Florentine Gardens, Hillhead, Glasgow; George Stanfield Blake, Purley Lodge, Purley, near Croydon; Edward Richards Bolton, 7, Leazes Terrace, Newcastle-on-Tyne; William Carter, 7, Victoria Street, Clitheroe; Henry Drysdale Dakin, 9, Beech Grove Terrace, Leeds; John Hanley, 4, Guion Road, Litherland, Liverpool; John Ansted Harrison, 47, London Road, Neath, Glamorganshire; Henry Herbert Higgs, 26, Anglesey Street, Lozells, Birmingham; Albert John Murphy, Preston House, Leeds; Arthur Theodore Neil, 21, South Grove, Highgate, N.; William Robertson, 41, Rosenau Road, Battersea Park, S.W.; Samuel Fenton Stell, 20, Henry Street, Keighley; George Edward Welch, 88, Caledonian Road, Leeds; Adam Storer Wylie, 93, Manchester Street, Oldham.

THE ADDRESS TO THE KING.

The PRESIDENT read the following Address, which the Council that afternoon had resolved to present to his Majesty the King. He moved that the Fellows of the Society should join with the Council in paying respect to the memory of the illustrious Queen they had so recently lost and in offering their homage to the new Sovereign. This was seconded by the TREASURER and carried unanimously, the Fellows all standing.

To His Most Gracious Majesty King Edward VII.

May it please your Majesty.

We, the President, Council, and Fellows of the Chemical Society, beg leave to approach your Majesty with expressions of deep sympathy in the grievous loss which your Majesty and the Empire have sustained through the death of our revered Sovereign, Queen Victoria, during whose beneficent reign the science of Chemistry, for the promotion of which her Majesty granted the Society a Royal Charter, has made immense progress.

We recall with gratitude the leading part which your illustrious Father, the Prince Consort, took in securing the extension of scientific knowledge in this country, and especially the great assistance he rendered in the foundation, in the year 1845, of the Royal College of Chemistry (since developed into the Royal College of Science), of which College he became the President.

We desire respectfully to congratulate your Majesty on your accession to the Throne, and most heartily to wish your Majesty a long, happy, and prosperous reign.

We venture to express the hope that your reign may be marked by discoveries in the science we represent not less brilliant than those which have characterised the reign of her late Majesty.

Signed on behalf of the Chemical Society,

T. E. THORPE, *President.*
W. A. TILDEN, *Treasurer.*
WYNDHAM R. DUNSTAN, } *Honorary*
ALEXANDER SCOTT, } *Secretaries.*
R. MELDOLA, *Foreign Secretary.*

THE DAY AND HOUR OF MEETING.

Mr. F. J. Lloyd asked whether the President could give any information as to the reasons which had led the Council to issue its recent circular requesting the views of the Fellows on a proposal to change the day and hour of the Ordinary Meetings of the Society.

The President, in reply, said that he was glad to take advantage of the opportunity which Mr. Lloyd had afforded him to state the attitude of the Council on the question. The expediency of an alteration in the day and hour of meeting had been mooted on more than one occasion, though no action was taken till the question was formally raised at a recent meeting of Council. The Secretaries were thereupon

directed to issue with the "Journal" for this month the circular and card referred to, with the view of eliciting the opinions of the Fellows upon the subject.

With respect to Mr. Lloyd's question as to the reasons for the inquiry, he might remind the Fellows that a great change had come over the social life of London during the fifty or sixty years of the Society's existence. A great number of what used to be called the 'resident' Fellows now lived in suburbs which were extending in all directions more and more widely. Moreover, the facilities for reaching town had been so enormously increased that it seemed worth while inquiring whether a rearrangement of the day and hour of meeting would render it possible for the country Fellows to attend the meetings of the Society in greater numbers than at present. He (the President) thought it would thus be seen that the Counci had good *primâ facie* grounds for testing the opinion of the general body of Fellows.

He might add that more than half of the cards issued had been returned, and of these a very large majority were in favour of the suggested alteration. No exact analysis had as yet been made, but the Fellows might be interested to know that those in favour of the change were in the ratio of about four or five to one. Of the 'resident' Fellows about two to two and a-half to one were in its favour. He expressed a wish that the remaining cards should be returned as quickly as possible so that the Council might have the opportunity of considering the replies, and of dealing with the matter, if necessary, at the Annual General Meeting.

A ballot for the election of Fellows was held and the following were subsequently declared duly elected:—

Andrew Charles Aitken, Thomas Stewart Barrie, John Cardew Bedwell, B.Sc., Herbert John Bult, Merrick W. Burrows, M.Sc., Robert Waley Cohen, B.A., Herbert H. Cousins, M.A., Gilbert Howard Daniel, B.Sc., Robert Dodd, Frederick G. Donnan, M.A., Ph.D., John Alfred Emery, Reginald W. Ferguson, Henry Edward Haddon, Arthur Houldershaw, Bernard Farmborough Howard, Edward Hughes, Robert Salmon Hutton, M.Sc., Stephen Archigenes Ionides, Major J. L. T. Jones, I.M.S., Robert Henry Jones, M.Sc., H. T. G. van der Linde, Nicholas Henry Martin, James Menzies, William Meredith, James Moir, M.A., B.Sc., Arthur W. Nunn, Theodore Henry Page, Thomas Slater Price, Ph.D., D.Sc., Lionel Guy Radcliffe, William Cecil Ramsden, Herbert Kilburn Scott, Harry Metcalfe Smith, John Talbot, B.A., B.Sc., Albert Edward Thomas, B.Sc., Major-Gen. J. Waterhouse, William A. Wayland, J. S. Wilson, M.D., C.M.

Of the following papers, those marked * were read:—

***8. "The action of hydrogen bromide on carbohydrates." By H. J. H. Fenton and Mildred Gostling.**

It was previously shown by the authors (*Trans.*, 1898, **73**, 554, and 1899, **75**, 423) that bromomethylfurfuraldehyde results when hydrogen bromide acts upon lævulose, sorbose, inulin, or cane sugar, and it was shown that the formation of this substance is characteristic of ketohexoses or of substances which give rise to them on hydrolysis. The experiments have now been extended, using a higher temperature and chloroform as the solvent. Under these conditions, all forms of *cellulose* give large yields of bromomethylfurfuraldehyde, and the results appear conclusively to prove that cellulose must contain a grouping or nucleus similar to that in lævulose. An account was also given of the behaviour of several other carbohydrates under similar conditions.

***9. "The ketonic constitution of cellulose." By C. F. Cross and E. J. Bevan.**

Having received a private communication of the results obtained by Fenton and Gostling, which are described in the preceding note, it has been deemed opportune to state fully the experimental evidence available for the solution of the problem of the constitution of cellulose.

For the view that cellulose is a near analogue of starch, that is, a polyanhydride of dextrose, the evidence is slender, resting mainly (1) on the well established empirical formula $(C_6H_{10}O_5)_n$ and (2) on the somewhat superficial study of the products of ultimate hydrolysis by Braconnot (*Ann.*, 1819, [ii], 12, 172) and Flechsig (*Zeit. Physiol. Chem.*, 1883, 7, 523).

The later evidence comprises the following items: (a) The tetracetate (Cross and Bevan) appears to be an ester of the unresolved cellulose (anhydride) with a formula $C_6H_6O\cdot(OAc)_4$, from which may be deduced as probable, the ketonic formula $CO{:}(CHOH)_4{:}CH_2$ for the cellulose unit; (b) Will and Lenze have shown (*Ber.*, 1898, **31**, 68) that the ketoses yield nitric esters with two ester groups less than the corresponding aldoses, two hydroxyl groups being condensed by internal reaction. Cellulose giving a trinitrate (C_6) with yields less than the theoretical (for the simple ester reaction) conforms with this general character of the ketoses and their anhydrides; (c) Faber and Tollens (*Ber.*, 1899, **32**, 2595), in a recent study of the oxycelluloses, have identified in the soluble products of the oxidation tartaric and oxalic acids and a dibasic acid containing five atoms of carbon. *Saccharic acid was not formed.* Further, the oxycelluloses digested with calcium hydroxide yield dioxybutyric and isosaccharic acids. Acids

with the normal six carbon chain are again conspicuously absent; (d) Brown and Morris (Trans., 1893, 63, 604) have established that cane-sugar is a first product of chlorophyllic assimilation and starch is probably only a derived overflow product. Further, that cane sugar, amongst the soluble carbohydrates, has a maximum nutritive value when tested in relation to chlorophyllic assimilation (Trans., 1890, 57, 484). A similar observation, but more directly with lævulose in relation to cellulose production, was made by A. Brown (Trans., 1886, 49, 432).

On the above grounds, the authors had previously concluded that cellulose is not a polyaldose (anhydride), but is of ketonic constitution.

Fenton and Gostling, by condensing cellulose to methylfurfural as a main reaction, have opened an entirely new direction of experimental attack, the first result of which is at least to render the polyaldose view of its constitution questionable.

Their results directly suggest that lævulose or other ketose is the raw material for cellulose elaboration and also offer a simple explanation of the origin of unsaturated compounds such as the furfural derivatives which are constituents of the lignone complex. It also further weakens the evidence upon which all furfural yielding constituents of plants have been assumed to be pentoses or pentosanes.

Discussion.

Dr. Horace Brown, whilst fully admitting that a considerable amount of evidence can now be brought forward in favour of the ketonic constitution of cellulose, expressed a doubt whether the small amounts of the bromo-derivative of methylfurfural obtained by Mr. Fenton from purified starches would justify the conclusion that starch contains the carbonyl group. More evidence is required of the specific nature of the reaction, and also of the absolute freedom of the starch from traces of "starch cellulose." He was unable to add anything to the physiological evidence put forward by Dr. Morris and himself some years ago, and which certainly did appear to lend some countenance to the view that in the plant economy lævulose has some genetic connection with cellulose rather than with starch.

Mr. Fenton said that although he and his colleague were at present concerned chiefly in demonstrating a ketonic grouping or nucleus in cellulose, he considered it not at all improbable that such a grouping exists, as a fraction of the whole, in the complex molecule of starch.

The product of hydrolysis of the portion containing such a grouping may very conceivably have been overlooked in the methods of identification hitherto employed.

***10. "Note on a method for comparing the affinity values of acids." By H. J. H. Fenton and H. O. Jones.**

In a former communication (*Trans.*, 1901, **79**, 92), the authors described a simple method for comparing the affinity values of acids based upon the decompositions of the hydrazone of oxalacetic acid. This substance when heated with pure water yields the hydrazone of pyruvic acid and carbon dioxide:

$$\begin{array}{l} CH_2CO_2H \\ C{:}N_2HPh \\ CO_2H \end{array} = \begin{array}{l} CH_3 \\ C{:}N_2HPh \\ CO_2H \end{array} + CO_2.$$

From 83 to 90 per cent. is decomposed in this manner, the slight differences observed in different specimens depending on their purity. But in presence of acids of sufficient concentration an entirely different change occurs; water is lost and Wislicenus' pyrazolone carboxylic acid is formed without evolution of any carbon dioxide:

$$\begin{array}{l} CH_2CO\cdot OH \\ C{:}N\cdot N\overset{H}{Ph} \\ CO_2H \end{array} = \begin{array}{l} CH_2\cdot CO \\ C{:}N\cdot NPh \\ CO_2H \end{array} + H_2O.$$

With acids of insufficient concentration both changes occur simultaneously, the amount of carbon dioxide evolved being less as the concentration of the acid increases. Making exactly parallel experiments with different acids, it was shown that the volumes of carbon dioxide obtained are in the inverse order of the affinity-values of the acids.

In order to explain the nature of this influence, the authors suggest that the undissociated molecule of the hydrazone tends only to lose water, giving the pyrazolone derivative, but that the negative ion $CO_2H - CN_2HPh - CH_2CO_2$ is unstable and tends to lose carbon dioxide. Upon this hypothesis any circumstance tending to prevent ionisation should favour the production of the pyrazolone derivative, and the presence therefore of a sufficient concentration of hydrogen ions should cause the change to take place in this direction more or less completely.

Other explanations might, of course, be offered, referring, for example, to the dehydrating influence of acids or to the 'basic' character of the pyrazolone ring, and it was therefore considered advisable to make further experiments in order to ascertain whether other conditions went in harmony with the ionisation hypothesis.

The investigations had reference to the influence of (a) salts, (b) non-electrolytes, (c) acids in presence of their own salts, and (d) solvents other than water.

In all the experiments the conditions were made exactly parallel, about 0·1 gram of the hydrazone being heated to 100° with 7·5 c.c. of the liquid to be examined in the manner previously described.

The solutions examined and results obtained were as follows :—

	Weight in grams in 100 c.c.	Weight of hydrazone.	Corrected volume of carbon dioxide.
1. Pure water		0·0998	8·31 c.c.
2. Sodium sulphate (cryst.)	6	0·1000	8·75 ,,
3. Cane sugar	6	0·1005	8·12 ,,
4. Urea	1	0·1000	8·31 ,,
5. Sulphuric acid	0·49	0·1003	2·60 ,,
6. Sulphuric acid and sodium sulphate	{0·49 / 6}	0·1000	7·12 ,,
7. Acetic acid	0·6	0·1001	7·07 ,,
8. Acetic acid and sodium acetate (cryst.)	{0·6 / 3}	0·1002	8·31 ,,
9. Amyl alcohol		0·0989	3·53 ,,
10. Toluene		0·1078	2·29 ,,
11. Nitrobenzene		0·1026	2·29 ,,

Bases likewise have practically no influence; thus 0·1001 gram hydrazone heated with a quantity of soda representing slightly *less* than 1 equivalent gave 8·58 c.c. (corr.) of carbon dioxide.

The conclusions which may be drawn from these experiments are :

(a) The influence of salts, bases, and non-electrolytes is *nil*, the results being practically identical with that given by pure water.

(b) The effect of a salt in presence of its own acid is greatly to diminish the influence of the acid, and

(c) Solvents having different ionising powers give very different results, the amount of carbon dioxide evolved being greatest in the case of water, less in amyl alcohol, and least in toluene and nitrobenzene.

With regard to the three last-named solvents, it may be remarked that, although they were carefully dried, water is produced in the pyrazolone formation, hence it is not surprising that some action should take place in a solvent such as toluene, which when pure has presumably little or no ionising power.

It is evident therefore that the results are, on the whole, well in harmony with the ionisation hypothesis, which certainly appears to offer the most satisfactory explanation of the phenomena, although other explanations are, of course, possible.

The purification of the hydrazone by recrystallisation is a troublesome and wasteful process, but the crude substance answers perfectly, since the results required are only relative. It is advisable to employ the same sample for each set of observations and the substance should be freshly prepared.

Discussion.

Dr. Travers remarked that the evolution of carbon dioxide from the acid seemed to take place under conditions similar to those which obtained during the electrolysis of the salt of an acid, and to be dependent on the concentration of the negative ion, in one case in the solution generally, and in the other on the surface of the anode. It would be interesting to know how the corresponding diphenylhydrazone would behave under similar conditions.

Mr. Fenton, in reply, said that one example of a disubstituted hydrazine had been investigated, namely, benzylphenylhydrazine, but that the oxalacetic derivative was extremely unstable, and only the pyruvic derivative could be isolated.

***11. "Organic derivatives of phosphoryl chloride, and the space configuration of the valencies of phosphorus." By R. M. Caven, B.Sc.**

By the interaction of ethoxyphosphoryl chloride, $OP\cdot OC_2H_5:Cl_2$ with two equivalents of aniline in ethereal solution, a chlorine atom is replaced and *ethoxyanilidophosphoryl chloride*, $OP\cdot OC_2H_5\cdot NHC_6H_5\cdot Cl$, results. This compound crystallises from ether in truncated pyramids, m. p. 61—62°. The remaining chlorine atom may be displaced by the action of *p*-toluidine, when the *ethyl ester* of *anilido*-p-*toluidophosphoric acid*, $OP\cdot OC_2H_5\cdot NHC_6H_5\cdot NHC_6H_4CH_3$, is obtained. This substance crystallises from dilute alcohol in needles, m. p. 116°.

p-Toluidine and aniline may be made to react in reverse order. Thus *ethoxy*-p-*toluidophosphoryl chloride* was obtained crystallised in oblique prisms, m. p. 74°; and the *ethyl ester* of p-*toluidoanilidophosphoric acid* was found to crystallise from dilute alcohol in needles, m. p. 116—117°.

The ethyl esters obtained by these reverse processes present similar physical and microscopic characters, and an intimate mixture of the two products melts at 116—117°. Thus the two compounds

$$OP\begin{cases} OC_2H_5 & (1) \\ NHC_6H_5 & (2) \\ NHC_6H_4CH_3 & (3) \end{cases} \quad \text{and} \quad OP\begin{cases} OC_2H_5 & (1) \\ NHC_6H_4CH_3 & (2) \\ NHC_6H_5 & (3) \end{cases}$$

are identical, and from this it appears that the two chlorine atoms in the compound $OP\cdot OC_2H_5\cdot Cl_2$ are similarly situated with regard to the rest of the molecule.

The only alternative to this would be the supposition that, the two chlorine atoms being differently situated, aniline and *p*-toluidine possess the power of appreciating this difference, and exercise a different pre-

dilection when reacting with the substance. This supposition, however, can hardly be entertained.

The chlorine atom replaced by the ethoxy-group might, however, differ in relative position from the other two chlorine atoms.

To determine whether this is so, aniline and *p*-toluidine were made to react directly with phosphoryl chloride, and the following compounds were obtained: *anilidophosphoryl chloride*, $OP{\cdot}NHC_6H_5{\cdot}Cl_2$, prisms, m. p. 79°; *anilido-p-toluidophosphoryl chloride*, $OP{\cdot}NHC_6H_5{\cdot}NHC_6H_4CH_3{\cdot}Cl$, very fine needles, m. p. 133—134°; *p-toluidophosphoryl chloride*, $OP{\cdot}NHC_6H_4CH_3{\cdot}Cl_2$, plates, m. p. 106°; *p-toluidoanilidophosphoryl chloride*, $OP{\cdot}NHC_6H_4CH_3{\cdot}NHC_6H_5{\cdot}Cl$, very fine needles, m. p. 133°. The two substances

$$OP\begin{cases}NHC_6H_5 & (1)\\ NHC_6H_4CH_3 & (2)\\ Cl & (3)\end{cases} \quad \text{and} \quad OP\begin{cases}NHC_6H_4CH_3 & (1)\\ NHC_6H_5 & (2)\\ Cl & (3)\end{cases}$$

present similar characteristics, and when mixed together melt at 133—134°. They are therefore identical.

It would seem then that the first and second chlorine atoms to be replaced are similarly situated, and therefore that all three chlorine atoms occupy similar positions within the molecule of phosphoryl chloride. The supposition that the chlorine atom which was at first replaced by the ethoxy-group refuses to react with bases, and is the particular atom which remains intact in these latter compounds, need scarcely be considered.

The above conclusion concerning the similarity of the chlorine atoms, if ultimately established, should be an important factor in settling the configuration of the phosphorus atom.

A tri-derivative, such as $OP\begin{cases}R^{I}\\ R^{II}\\ R^{III}\end{cases}$, in which the points of attachment of the three radicles are similarly situated in space with reference to the rest of the molecule, does not contain a plane of symmetry. It should therefore be capable of existing in right- and left-handed forms in which the phosphorus atom is the centre of optical activity. Experiments are now in progress to determine this point, and the fact that one of the elements is doubly bound to the phosphorus atom lends additional interest to the investigation, which was commenced at the suggestion of Dr. Kipping.

*12. "α-Hydroxycamphorcarboxylic acid." By A. Lapworth and E. M. Chapman.

An account was given of experiments begun with the view of preparing α-bromohomocamphoric acid, an object which has been achieved in another way (*Trans.*, 1900, **77**, 1063).

A method for preparing camphorquinone in large quantities, and free from camphoric anhydride, was described. *Camphorquinone-p-bromophenylhydrazone*, $C_{10}H_{14}O{:}N_2H{\cdot}C_6H_4Br$, is eminently suited for the detection of the quinone in small quantities; it is very sparingly soluble in nearly all organic media, and melts at 215—216°. It appears to exist only as the ketonic modification (Betti, *Ber.*, 1899, **32**, 1995). *Camphorquinonesemicarbazone*, $C_{10}H_{14}O{:}N_2H{\cdot}CONH_2$, which is nearly colourless at ordinary temperatures, turns yellow at 210°, melts and decomposes at 228—229°.

When camphorquinone is treated with hydrogen cyanide at −10°, a nearly colourless mass is produced, which probably consists of stereoisomeric forms of *α-dihydroxycyanocamphor*, $C_8H_{14}<\begin{matrix}C(OH)CN\\CO\end{matrix}$. One of these was isolated in the form of six-sided plates, which decomposed when heated, and melted at 197—198°, approximately the melting point of camphorquinone; it had all the properties of an α-hydroxynitrile, and when dissolved in fuming sulphuric acid was converted into *α-hydroxycamphorcarboxylic amide*, $C_8H_{14}<\begin{matrix}C(OH)CONH_2\\CO\end{matrix}$, which forms large, brilliant crystals melting, somewhat indefinitely, at 235—240°.

α-Hydroxycamphorcarboxylic acid, $C_8H_{14}<\begin{matrix}C(OH)CO_2H\\CO\end{matrix}$, is formed on heating the nitrile with strong hydrobromic acid for some time. It is sparingly soluble in water, and crystallises in brilliant needles or prisms which melt and decompose at 207—208°, becoming converted into Manasse's hydrocamphor (*Ber.*, 1897, **30**, 659). The acid is converted into carbon dioxide and camphorquinone by lead peroxide and acetic acid, and is slowly decomposed when heated with alkalis, being, perhaps, converted into *dia*-homocamphanic acid (*Trans.*, 1900, **77**, 1067). *α-Acetoxycamphorcarboxylic acid*, $C_8H_{14}<\begin{matrix}C(OAc)CO_2H\\CO\end{matrix}$, melts at 85—86°.

It was pointed out that these compounds must contain the carboxyl group in the position in which it occurs in camphor.

***13. "The bacterial decomposition of formic acid." By W. C. C. Pakes and W. H. Jollyman.**

The authors, as the result of various observations, were led to analyse the gases produced from sodium formate in solution by certain bacteria. These experiments show that hydrogen and carbon dioxide are evolved, sodium hydrogen carbonate remaining in the medium in which the sodium formate was dissolved. The total amount of carbon dioxide, that is, the amount evolved as a gas and that in combination, was found to be equal in volume to the amount of hydrogen evolved. It is therefore possible to express the reaction by a very simple equation, either $H{\cdot}CO_2Na + H_2O = NaHCO_3 + H_2$ or $H{\cdot}CO_2H = CO_2 + H_2$. One of the chief reasons why the addition of sodium formate to media containing dextrose is of such advantage is that the alkali formed from the decomposition of the sodium formate neutralises the acids produced by the decomposition of the sugar; the fact that the medium continues to be neutral or alkaline allows the bacteria to grow for a longer period than when the medium becomes increasingly acid.

Many bacteria had no action upon the formate, and it was found that none of the more commonly occurring yeasts had any action upon the salt.

14. "Preparation of substituted amides from the corresponding sodamide." By A. W. Titherley, M.Sc., Ph.D.

The behaviour of sodamide derivatives of the type $R{\cdot}CO{\cdot}NHNa$ with various halogen organic compounds was investigated, when the marked difference observed between the aliphatic and aromatic derivatives suggested a dissimilarity in their constitution.

(a) With alkyl haloids. In presence of benzene there is no action; alcohol, if present, takes part in the reaction, giving the amide and an ether, thus: $CH_3{\cdot}CO{\cdot}NHNa + C_2H_5OH + C_2H_5I = CH_3CO{\cdot}NH_2 + NaI + C_2H_5OC_2H_5$. Sodiobenzamide in sealed tubes at 140° readily gives alkyl derivatives, $C_6H_5CO{\cdot}NHR$, in absence of alcohol, whilst sodacetamide under similar conditions undergoes complex decomposition, giving only a small quantity of the alkylacetamide.

(b) With acid chlorides in presence of benzene, sodiobenzamide behaves normally, giving diamides, $C_6H_5CO{\cdot}NH{\cdot}COR$, but sodacetamide does not give regular results. With acetyl chloride, diacetamide is formed, but with benzoyl chloride a complex change takes place, dibenzamide, tribenzamide, acetamide, diacetamide, benzonitrile, and benzoic anhydride being formed, but no acetyl benzamide.

(c) With halogen esters, sodiobenzamide behaves normally, but gives only small yields of direct condensation products. Ethyl

hippurate was synthesised by the action of ethyl bromacetate on sodiobenzamide. Sodacetamide gives unsatisfactory results.

(d) With bromamides, symmetrical disubstituted acyl hydrazines were expected, in accordance with the equation $R{\cdot}CO{\cdot}NHNa + R{\cdot}CO{\cdot}NHBr = R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}R + NaBr$; but no trace of these substances was obtained, as both aliphatic and aromatic derivatives immediately undergo molecular rearrangement, giving alkyl acyl ureas, $NHR{\cdot}CO{\cdot}NH{\cdot}COR$.

It was found that the sodium atom could be best replaced by alkyl radicles by heating with potassium alkyl sulphates; for example:

With sodamide, amines are formed thus:

$$NaNH_2 + KRSO_4 = R{\cdot}NH_2 + KNaSO_4.$$

With sodium organic amides, substituted amides are formed:

$$CH_3{\cdot}CO{\cdot}NHNa + KRSO_4 = CH_3{\cdot}CO{\cdot}NHR + KNaSO_4.$$

On treatment with sodamide, the remaining hydrogen atom in the group CONHR may be replaced by sodium, and this similarly replaced by an alkyl group. The stages are:

$$R{\cdot}CO{\cdot}NH_2 \longrightarrow R{\cdot}CO{\cdot}NHNa - R{\cdot}CO{\cdot}NHR^{I} \longrightarrow R{\cdot}CO{\cdot}NNaR^{I} \longrightarrow R{\cdot}CO{\cdot}NR^{I}R^{II},$$

where R^{I} and R^{II} may be similar or dissimilar radicles.

Several new monalkyl amides and mixed dialkyl amides have been thus prepared, and their behaviour, with dry hydrochloric acid and sodamide respectively, studied. The hydrochlorides of the monalkyl amides contain base and acid in the proportion of 1 mol. : 1 mol. (compare acetamide hydrochloride), and in the aliphatic group are solid, crystalline, very easily fusible, fairly stable substances; in the aromatic group, thick viscid liquids, which dissociate readily.

Acetethylamide hydrochloride, $CH_3{\cdot}CO{\cdot}NHC_2H_5,HCl$, melts at 60°; and *acet-n-propylamide hydrochloride*, $CH_3{\cdot}CO{\cdot}NHC_3H_7,HCl$, melts at 47°; *acetisobutylamide*, $CH_3{\cdot}CONH{\cdot}C_4H_9^{\beta}$, is a liquid boiling at 225—227°, is miscible with water, but is readily separated as an oil by adding alkali; its hydrochloride melts at 107°.

Benz-n-proylamide, $C_6H_5{\cdot}CO{\cdot}NHC_3H_7$, crystallises in cubic-shaped crystals melting at 84·5°, and boiling at 294—295°.

Benzbutylamide, $C_6H_5{\cdot}CO{\cdot}NHC_4H_9$, melts at 57°, and boils with slight decomposition at 295—296°. *Acetmethylethylamide*, $CH_3{\cdot}CO{\cdot}N(CH_3)C_2H_5$, boils at 180°; and *benzmethylethylamide*, $C_6H_5{\cdot}CO{\cdot}N(CH_3)C_2H_5$, boils at 280°. Both are liquids. The sodium derivatives, $R{\cdot}CO{\cdot}NNaR^{I}$, are white powders, appreciably soluble in benzene. In the aliphatic series they dissolve unchanged in alcohol, and the solutions give, with alcoholic silver nitrate, *orange* precipitates. The aromatic sodium alkyl amides are decomposed by alcohol.

The author discussed the tautomerism of the amides and expressed the view that in the aliphatic group the sodium compounds are true sodamide derivatives of the type R·CO·NHNa, whilst in the aromatic group they are partly sodium salts of the imidohydroxy-formula, $R\cdot C\lessdot^{NH}_{ONa}$, and partly R·CO·NHNa. Two series of silver derivatives have been obtained, one white, presumably $R\cdot C\lessdot^{NH}_{OAg}$, and the other orange, $R\cdot C\lessdot^{O}_{NHAg}$, which are capable of passing into each other and are very unstable.

The formula of benzamide itself in aqueous solution is probably $C_6H_5\cdot C\lessdot^{NH}_{OH}$, and that of acetamide, $CH_3\cdot CO\cdot NH_2$.

15. "**Note on two molecular compounds of acetamide.**" **By A. W. Titherley, M.Sc., Ph.D.**

Acetamide sodium bromide, $2CH_3\cdot CONH_2,NaBr$, and acetamide sodium iodide, $2CH_3\cdot CONH_2,NaI$, are well defined crystalline compounds analogous to the hydrochloride, $2CH_3\cdot CONH_2,HCl$. They were obtained as bye-products in certain reactions, and may be prepared by direct union of the constituents in the presence of alcohol. On concentration or cooling they separate as needles which begin to dissociate below their melting points and are very deliquescent. On quickly heating, $2CH_3\cdot CONH_2,NaBr$ melts at 144° with separation of NaBr, and $2CH_3\cdot CONH_2,NaI$ melts at 110° with separation of NaI. Molecular compounds with other haloid compounds of potassium and sodium do not appear to exist.

16. "**Diacetamide; a new method of preparation.**" **By A. W. Titherley, M.Sc., Ph.D.**

Diacetamide may be readily prepared by the direct action of acetyl chloride (in benzene solution) on acetamide, $3CH_3CONH_2 + CH_3COCl = (CH_3CO)_2NH + 2(CH_3\cdot CONH_2)HCl$. After filtering off the insoluble acetamide hydrochloride and removing the benzene by distillation, the residue is fractionated. No previous account appears to have been given of this reaction.

Neither acetyl nor benzoyl chloride has any action on benzamide, but the benzoyl chloride gradually decomposes acetamide, with formation of benzoic acid, benzoic anhydride and acetonitrile.

17. "Organic derivatives of silicon." By F. S. Kipping and L. L. Lloyd.

Experiments on the preparation of enantiomorphously related silicon compounds were commenced nearly three years ago, and a short account of this work has already appeared (*Proc.*, 1899, **15**, 174); the much more important object, the separation of the isomerides, has not yet been attained.

When silicon tetrachloride is treated in dilute ethereal solution with one molecular proportion of a phenol or alcohol, it is decomposed in accordance with the equation $SiCl_4 + R^I \cdot OH = SiCl_3 \cdot OR^I + HCl$, and by submitting the product to a similar treatment, a second group, and then a third may be introduced,

$$SiCl_3 \cdot OR^I + R^{II} \cdot OH = SiCl_2(OR^I)(OR^{II}) + HCl$$
$$SiCl_2(OR^I)(OR^{II}) + R^{III} \cdot OH = SiCl(OR^I)(OR^{II})(OR^{III}) + HCl.$$

Amido-compounds may be used in the above reactions in the place of alcohols or phenols with similar results.

Phenoxymethoxysilicon dichloride, $SiCl_2(OPh)(OMe)$ (b. p. 216°), and *phenoxymethoxyethoxysilicon chloride*, $SiCl(OPh)(OMe)(OEt)$ (b. p. 241°), are colourless, oily liquids readily decomposed by water; *methoxyethoxysilicon dichloride*, $SiCl_2(OMe)(OEt)$, and *methoxyethoxyisobutoxysilicon chloride*, $SiCl(OMe)(OEt)(OBu^\beta)$, boiling at 128° and 160° respectively, have similar properties.

The principle on which the above reactions are based, namely, the interaction of halogen compounds and hydroxylic or amido-derivatives, is evidently capable of general application, and its use for the preparation of enantiomorphously related compounds is being investigated by one of us in the case of elements other than silicon.

18. "Isomeric hydrindamine camphor-π-sulphonates. Racemisation of α-bromocamphor." By F. S. Kipping.

In examining the salt formed by the combination of *d-l*-hydrindamine with *d*-camphor-π-sulphonic acid (obtained by the reduction of α-bromocamphorsulphonic acid) in order to try and isolate isomeric salts analogous to those obtained from the bromo-acid (*Trans.*, 1900, **77**, 861), it was found that although the salt at first seemed to be homogeneous, it could be resolved into fractions having different specific rotations.

This difference in optical properties is due to the fact that the crude *d*-camphor-π-sulphonic acid contains a very small quantity of the enantiomorphously related isomeride, and as the latter can hardly have been produced during the reduction of the bromocamphorsulphonic

acid, it follows that α-bromocamphor undergoes partial racemisation during sulphonation.

This change is one of considerable complexity, and necessitates the transference of part of one of the closed chains in bromocamphor from one position to another, as in the case of the optical inversion of camphor (Kipping and Pope, *Trans.*, 1897, 71, 958).

Except for the separation already referred to, the salt of *d-l*-hydrindamine with camphor-π-sulphonic acid undergoes no change on fractional crystallisation, and gives a molecular rotation practically identical with that of ammonium *d*-camphor-π-sulphonate; it is, therefore, a *partially* externally compensated salt of the type *d*A*l*B,*d*A*d*B; it crystallises from water in large transparent rhomboidal prisms containing water of crystallisation, and melts at about 198°.

19. "Tetramethylene carbinol." By W. H. Perkin, jun.

When the chloride of tetramethylenecarboxylic acid is reduced in moist ethereal solution with sodium, it is converted into tetramethylene carbinol, $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH\cdot CH_2OH\end{matrix}$, a colourless oil boiling at 143—144° and having an odour resembling that of isoamyl alcohol. The determinations of the density, refraction and magnetic rotation of this substance are given in the etailed paper.

ANNIVERSARY DINNER.

It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Wednesday, March 27th, 1901, the day preceding that fixed for the Annual General Meeting. Further particulars will shortly be announced.

At the next meeting, on Thursday, February 21st, the following papers will be communicated :

"Isomeric hydrindamine mandelates and phenylchloracethydrindamides." By F. S. Kipping and H. Hall.

"Isomeric benzylhydrindamine bromocamphorsulphonates and some salts of *d-l*-hydrindamine." By F. S. Kipping and H. Hall.

"Condensation of phenols with esters of the acetylene series. IV. Benzo-γ-pyrone and its homologues." By S. Ruhemann and H. W. Bausor.

"Constitution of bromocamphoric anhydride and camphanic acid." By A. Lapworth and W. H. Lenton.

"The action of acetylchlor- and acetylbrom-aminobenzenes on amines and phenylhydrazine." By F. D. Chattaway and K. J. P. Orton.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

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February 21st, 1901. Dr. ARMSTRONG, Vice-President, in the Chair.

Messrs. Hugh Ramage, R. W. Cohen, and A. W. Nunn, were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Edward George Paul Bousfield, St. Swithin, Hendon; Albert Ernest Dunstan, 24, Lidfield Road, Stoke Newington, N.; Alfred James Hyder, 22, Gunton Road, Upper Clapton, London, N.E.; William Henry Coutts Jemmett, Tintern, Gap Road, Wimbledon; William Shepperson, Longfield, Gt. Missenden, Bucks; Charles Edmund Shaw Sherratt, 24, Argyll Road, Normacott, Staffs.

It was announced that the following changes in the Officers and Council were proposed by the Council:

As *President*: Professor J. Emerson Reynolds, Sc.D., M.D., F.R.S., *vice* Professor T. E. Thorpe, C.B., Ph.D., D.Sc., LL.D., F.R.S.

As *Vice-Presidents*: Professor Herbert McLeod, F.R.S., and Professor H. A. Miers, M.A., F.R.S., *vice* Professor G. D. Liveing, M.A., F.R.S., and Professor J. M. Thomson, LL.D., F.R.S.

As *Ordinary Members of Council*: Dr. A. W. Crossley, Professor J. J. Dobbie, M.A., D.Sc., Dr. M. O. Forster, and Mr. S. U. Pickering, M.A., F.R.S., *vice* Professor J. Norman Collie, Ph.D., F.R.S., Mr. Gowland, Mr. C. T. Heycock, M.A., F.R.S., and Dr. Messel.

Mr. F. J. M. Page, Mr. E. W. Voelcker and Mr. A. C. Chapman were appointed to audit the Society's accounts.

Mr. F. J. Lloyd was appointed to act with the Officers and Dr

Chattaway, who had been appointed by the Council, in drawing up a Report to the Council on the replies which have been received to the question as to the suggested change in the day and hour of the Ordinary Meetings.

Of the following papers, those marked * were read :

***20. "Isomeric hydrindamine mandelates and phenylchloroacethydrindamides." By F. S. Kipping and H. Hall.**

Although many salts of *d*-*l*-hydrindamine with different optically active acids have now been submitted to fractional crystallisation (Kipping, *Trans.*, 1900, 77, 861), the resolution of the base into enantiomorphously related compounds has not yet been accomplished; this fact, and the formation in some cases of isomeric salts which appear to be partially racemic, led the authors to try to obtain some direct evidence of the asymmetry of the base.

The fractional crystallisation of d-l-*hydrindamine* d-l-*mandelate*, $C_9H_{11}N,C_8H_8O_3$, was therefore undertaken in order to ascertain whether the two racemic or externally compensated salts,

*d*B*d*A, *l*B*l*A, and *d*B*l*A, *l*B*d*A,

could be separated, but the several fractions proved to be identical, owing possibly to the conversion of one isomeride into the other,

*d*B*d*A,*l*B*l*A $\rightleftarrows$ *d*B*l*A,*l*B*d*A.

From *d*-*l*-hydrindamine and *d*-*l*-phenylchloroacetyl chloride, however, two isomeric *phenylchloroacethydrindamides*, $C_6H_5{\cdot}CHCl{\cdot}CO{\cdot}NH{\cdot}C_9H_9$, melting at 150—151° and 124—125° respectively, were obtained; in this case, the isomerides are not mutually convertible in solution, and their formation shows that the base is externally compensated.

d-l-*Hydrindamine* d-*mandelate*, prepared from the pure *d*-acid, is not resolved into different fractions when it is crystallised from alcohol; it is therefore a partially externally compensated salt, *d*A*l*B, *d*A*d*B.

The hydrindamine salts derived from racemic mandelic acid and from pure *d*-mandelic acid respectively are indistinguishable except in optical properties; they both melt at 139—141°, whether heated separately or mixed together in different proportions; they have also the same, or almost the same solubility, for when a mixture of the two is fractionally crystallised, the several deposits have practically the same specific rotations.

It may be concluded, therefore, that the three optically different compounds, *d*A*d*B, *d*A*l*B, *l*A*l*B, form isomorphous mixtures, and that

the salts of the active and inactive acids do not represent true partially racemic or racemic compounds.

The use of externally compensated acid chlorides for the detection of asymmetry, and of the active chlorides for the separation of enantiomorphously related compounds, is being further investigated.

***21. "Isomeric benzylhydrindamine bromocamphorsulphonates, and some salts of *d-l*-hydrindamine." By F. S. Kipping and H. Hall.**

Benzylhydrindamine, $C_9H_9{\cdot}NH{\cdot}C_7H_7$, prepared by treating *d-l*-hydrindamine with benzyl chloride, unites with *a*-bromocamphorsulphonic acid, forming a mixture of two isomeric salts, $C_{16}H_{17}N,C_{10}H_{14}BrO{\cdot}SO_3H$, which are separable by fractional crystallisation.

The more sparingly soluble "*α*-salt" forms transparent plates, melts at 206—207°, and has a specific rotation $[\alpha]_D = +50°$ in ethyl alcohol.

The more readily soluble "*β*-salt" crystallises in ill-defined prisms, melts at 186—187°, and has a specific rotation $[\alpha]_D = +51{\cdot}5°$ in ethyl alcohol; in chloroform, the specific rotation of the *β*-salt seems to be slightly greater than that of the isomeride.

Both salts give an optically inactive base when decomposed with barium hydroxide solution, and they both contain an acid optically identical with ordinary *d*-*α*-bromocamphorsulphonic acid. Since they both contain an asymmetric carbon group, as well as a nitrogen atom which is directly united with (H),(C_9H_9),(C_7H_7), and with the ion of the bromo-acid, they might be regarded as salts of the two different externally compensated bases, $+C+N^v$, $-C-N^v$, and $+C-N^v$, $-C+N^v$, or they may be considered to be analogues of the isomeric hydrindamine bromocamphorsulphonates, &c., which have been recently described (Kipping, *Trans.*, 1900, **77**, 861).

d-l-*Hydrindamine* d-*camphorsulphonate*, $C_9H_{11}N,C_{10}H_{15}O{\cdot}SO_3H$, prepared from the base and Reychler's camphorsulphonic acid, like the salt obtained with *d*-camphor-*π*-sulphonic acid, is not resolved into isomerides on fractional crytallisation; it forms long prisms melting at 165—166°, and is very readily soluble in water.

d-l-*Hydrindamine* d-*hydroxy*-cis-*π*-*camphanate*, $C_9H_{11}N,C_{10}H_{14}O_5$, unlike the corresponding salt of *l-cis-π*-camphanic acid, also remains homogeneous on fractional crystallisation; it forms transparent prisms ($+\frac{1}{2}H_2O$) melting at 202—203°.

***22. "Constitution of bromocamphoric anhydride and camphanic acid." By A. Lapworth and W. H. Lenton.**

The fact that ordinary bromocamphoric anhydride on treatment with alkalis is in part converted into lauronolic acid by loss of hydro-

gen bromide and carbon dioxide has led to the view that the bromine atom is in the β-position with regard to one of the carboxyl groups (Aschan, *Ber.*, 1894, **27**, 2112), as it is with β-bromo-acids that this property is almost exclusively associated.

In the belief that the behaviour of the anhydride in this respect is misleading, the authors have made numerous experiments which have resulted in the following observations.

Camphanic acid, on treatment with phosphorus pentabromide, is reconverted into bromocamphoric anhydride, showing that the lactonic oxygen atom occupies the position of the bromine atom in the anhydride.

It is difficult to oxidise camphanic acid with any but powerful agents, and when attacked it is usually converted into camphoronic acid or its decomposition products. When its amide, however, is warmed with phosphorus chlorides it is converted into the nitrile, and this, on treatment with alkalis, is at once resolved into hydrogen cyanide and camphononic acid, which, apart from all views as to the constitution of camphor, must have the structure $CO_2H\cdot CMe\langle^{CMe_2\cdot CO}_{CH_2-CH_2}$.

Camphanonitrile is therefore the lactone of an α-hydroxynitrilic acid, namely, $\begin{matrix}CH_2\cdot CMe-CO\\ |\quad\ CMe_2\quad |\\ CH_2\cdot C(CN)\cdot O\end{matrix}$, which would decompose on treatment with alkalis in the above manner. Camphanic acid and bromocamphoric anhydride are therefore represented by the formulæ suggested by Bredt, namely, $\begin{matrix}CH_2\cdot CMe-CO\\ |\quad\ CMe_2\quad |\\ CH_2\cdot C(CO_2H)\cdot O\end{matrix}$ and $\begin{matrix}CH_2\cdot CMe-CO\\ |\quad\ CMe_2\quad O\ |\\ CH_2\cdot C(Br)\cdot CO\end{matrix}$, and the formation, from them, of lauronolic acid has not the significance which has been attached to it.

***23. "The action of acetylchloro- and acetylbromo-aminobenzenes on amines and phenylhydrazine." By F. D. Chattaway and K. J. P. Orton.**

In studying the action of nitrogen chlorides and nitrogen bromides on amines and phenylhydrazine, the authors have used the acetylchloro- and acetylbromo-amino-2 : 4-dichlorobenzene recently prepared by them, as these substances are readily obtained pure. The operations have generally been carried out in chloroform solution, avoiding as far as possible the presence of water.

The reaction with the aliphatic amines is represented by the equation $R\cdot NH_2 + C_6H_3Cl_2\cdot NClAc = R\cdot NHCl + C_6H_3Cl_2\cdot NHAc$. The chloro-amino-derivatives thus formed can be isolated.

The initial reaction with the aromatic amines (anilines and toluidines) is similar. The halogen, however, immediately wanders from the nitrogen into the para- and ortho-positions if these are unoccupied When the hydrogen atoms in the positions 2, 4, and 6 are already substituted, no such intramolecular transformation can take place, but the halogen amino-derivatives of such anilines (as *s*-trichloroaniline) are very unstable, and decompose, yielding substituted azobenzenes. The azo-formation takes place to some extent when acetylchloroaminobenzenes react with the less substituted anilines and toluidines.

Two reactions take place between phenylhydrazine and halogen amino-compounds. The one, when phenylhydrazine is in excess, is represented by the equation $4C_6H_5\cdot NH\cdot NH_2 + 2(:NX) = C_6H_5N_3 + C_6H_5NH_2 + 2C_6H_5\cdot NH\cdot NH_2\cdot HCl + 2(:NH)$; the other, when the halogen amino-compound is in excess, by the equation $C_6H_5NH\cdot NH_2 + 3(:NX) = C_6H_5X + N_2 + X_2 + 3(:NH)$.

In the authors' opinion, the formation of these substances is not a result of oxidation, but depends on the intermediate formation of halogen hydrazino-derivatives.

The following hitherto undescribed substances have been prepared: *Aceto-4-chloromethylaniline*, $C_6H_4Cl\cdot NCH_3\cdot COCH_3$, m. p. 92°, white plates from petroleum; *o-chloromethylaniline*, $C_6H_4Cl\cdot NH\cdot CH_3$, a colourless oil, b. p. 218° (760 mm.); *2-chloro-5-bromoacetanilide*, $C_6H_3ClBr\cdot NH\cdot COCH_3$, needles, m. p. 141°; *3-bromo-4-chloroacetanilide*, $C_6H_3ClBr\cdot NH\cdot COCH_3$, rhombs, m. p. 130°; *2 : 4 : 6, 2′ : 4′ : 6′-hexachloroazobenzene*, $C_6H_2Cl_3\cdot N:N\cdot C_6H_2Cl_3$, dark red needles, m. p. 188°.

***24. "The preparation of orthochloroaniline." By F. D. Chattaway and K. J. P. Orton.**

The authors described a convenient method of preparing orthochloroaniline by the chlorination of acetanilide.

The chlorination is effected by adding the calculated quantity of a strong solution of bleaching powder to a solution of acetanilide (1 part) in glacial acetic acid (3 to 4 parts). Orthochloroacetanilide, which forms from 5 to 8 per cent. of the product, is partly separated from the para-derivative by fractional crystallisation from alcohol. The *o*-chloroaniline is finally freed from *p*-chloroaniline by distilling in steam from sulphuric acid.

***25. "The bacterial oxidation of formates by nitrates." By W. C. C. Pakes and W. H. Jollyman.**

In previous communications the authors have described the actions of a group of bacteria upon solutions containing sodium formate, and

of another group upon solutions containing sodium or potassium nitrate.

Many of the bacteria which decompose the formate are also found to decompose the nitrate, such, for instance, as the *B. coli communis*, *B. enteritidis* of Gärtner, and the *Pneumobacillus* of Friedländer, each of which converts formic acid into carbon dioxide and hydrogen, and reduces nitric to nitrous acid.

If any of these bacteria be cultivated in a medium containing both formate and nitrate (1 per cent. of each), it will be found that no gas will be evolved. After the lapse of several days, the fluid will be found to contain sodium hydrogen carbonate and sodium nitrite. When the medium contains an excess of sodium formate as compared with the sodium nitrate, gas is evolved which, upon analysis, proves to consist of carbon dioxide and nitrogen.

When the same bacteria are cultivated in media containing *d*-glucose and sodium nitrate, a similar effect is produced, gas is evolved which consists of carbon dioxide and nitrogen, or carbon dioxide, nitrogen and hydrogen, the latter being found if the sugar is in excess as compared with the nitrate.

The authors have not yet been able to determine whether a similar result would be obtained when the organism used did not act upon both, but they have succeeded in showing that the *B. pyocyaneus* (which does not decompose formate) acts in a medium containing both salts almost as if the formate were absent; they have not as yet been able to find a bacterium which decomposes formate, but which does not reduce nitrates.

26. "Condensation of phenols with esters of the acetylene series. Part IV. Benzo-γ-pyrone and its homologues." By S. Ruhemann and H. W. Bausor, B.A.

Ruhemann and Stapleton have shown (*Trans.*, 1900, **77**, 1184) that phenoxyfumaric acid under the influence of concentrated sulphuric acid condenses to benzo-γ-pyronemonocarboxylic acid, which, on distillation, yields benzo-γ-pyrone. The authors of the present paper have applied these reactions to the cresoxyfumaric acids, and thus obtained the corresponding tolu-γ-pyronecarboxylic acids and tolu-γ-pyrones.

27. "The influence of solvents on the rotation of optically active compounds. II. The influence of isobutyl alcohol and secondary octyl alcohol (methylhexylcarbinol) on the rotation of ethyl tartrate. By T. S. Patterson.

In continuation of work already published (*Trans.*, 1901, **79**, 167), experiments were described whose object was to determine the in-

fluence of *iso*butyl and octyl alcohols as solvents upon the rotation of ethyl tartrate. It was found that both liquids lower the specific rotation of the dissolved active substance, the latter having the greater effect. In both cases, concentrations of distinct minimum rotation occur. This phenomenon was briefly discussed.

It was also shown that ethyl tartrate in *iso*butyl alcohol has a molecular-solution-volume greater than that in *n*-propyl alcohol, but less than that in octyl alcohol, which is in agreement with the generalisation deduced from the results of the former investigation.

28. **"Influence of a heterocyclic group on optical rotation; the ethyl and methyl salts of dipyromucyltartaric acid." By P. F. Frankland and F. W. Aston.**

The authors have investigated the influence on optical rotation of the heterocyclic furfurane group by preparing diethyl dipyromucyltartrate and determining its rotation. The molecular rotation, $[M]_D^{20} = -321{\cdot}44°$, $[M]_D^{99{\cdot}5} = -266{\cdot}54°$, is, at 20°, intermediate between that of diethyl di-*m*-toluyltartrate ($[M]_D^{20} = -306{\cdot}3°$) and diethyl di-*p*-toluyltartrate ($[M]_D^{20} = -484{\cdot}4°$), and at 100° intermediate between that of diethyl dibenzoyltartrate ($[M]_D^{100} = -251{\cdot}6°$) and diethyl di-*m*-toluyltartrate ($[M]_D^{100} = -281{\cdot}7°$). Thus the influence of the pyromucyl radicle is similar to that of the aromatic acid, but unlike that of the fatty acid radicles, the derivatives of ethyl tartrate with two equivalents of the former being strongly lævorotatory whilst those with the latter are more strongly dextrorotatory than ethyl tartrate itself. The pyromucyl derivative again resembles the corresponding aromatic derivatives in having its lævorotation diminished by rise of temperature, whilst the corresponding derivatives with fatty acid radicles have their dextrorotation increased under the same circumstances.

The authors also described a novel method of continuous automatic esterification which has been advantageously employed by them in the preparation of methyl and ethyl tartrates.

ANNIVERSARY DINNER.

It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Wednesday, March 27th, 1901, the day preceding that fixed for the Annual General Meeting. Further particulars will shortly be announced.

At the next meeting, on Thursday, March 7th, the following papers will be communicated:

"Nomenclature of the acid esters of unsymmetrical dibasic acids." By J. J. Sudborough.

"Additive compounds of α- and β-naphthylamine with trinitrobenzene derivatives." By J. J. Sudborough.

"Acetylation of arylamines." By J. J. Sudborough.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 234.

March 7th, 1901. Dr. PERKIN, F.R.S., Vice-President, in the Chair.

Messrs. T. H. Page and James Moir were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Ernest Clark, 9, Polygon Avenue, Stockport Road, Manchester; Thomas Kennedy Cockburn, 26, Elm Street, Whiteinch, Glasgow; Eustace Coddington, 131, St. James' Road, Upper Tooting, London, S.W.; Hugh Edward Ellis, 18, Belmont Road, Aberdeen; John Vargas Eyre, 26, Bridge Road West, Battersea Park, S.W.; Francis Robert Henley, Watford, Rugby; Charles Edward Kenneth Mees, 33, St. Saviour's Road, Croydon; Arthur Peacock, Smithies Bridge House, Heckmondwike, Yorks.; William Hammond Robinson, The Limes, Painswick Road, Cheltenham; Henry Ewing Smith, 22, City Road, London, E.C.; William Henry Taylor, 19, Shafton Road, Victoria Park Road, N.E.

Of the following papers, those marked * were read:

***29. "Nomenclature of the acid esters of unsymmetrical dicarboxylic acids." By J. J. Sudborough.**

After mentioning the systems adopted by Brühl, Wegscheider, and Anschütz, the author suggested the following nomenclature.

Of the two isomeric monoalkyl esters of an unsymmetrical dibasic acid, that ester be termed the α-compound which has the higher esteri-

fication constant, and the other with the lower constant the β-compound.

The advantages of this system are: (1) similarly constituted esters receive similar names; (2) in the case of many of the simpler acids, the substituent which produces the want of symmetry is in the α-position to the alkylated carboxylic group; (3) ease with which the two esters may be identified.

***30. "Additive compounds of α- and β-naphthylamine with trinitrobenzene derivatives." By J. J. Sudborough.**

The red needles which were obtained when α-naphthylamine trinitrobenzoate was boiled with alcohol (*Trans.*, 1899, 75, 588) are an additive compound of trinitrobenzene with α-naphthylamine. A number of other similar compounds have been obtained; all are red or reddish-purple in colour, are remarkably stable, may be crystallised from glacial acetic acid, and are only slowly decomposed by cold dilute hydrochloric acid; they are also stable when exposed to the air, and in these properties differ from the additive compounds of trinitrobenzene, with aniline, toluidine, &c., described by Hepp (*Annalen*, 1882, 215, 344).

The following are the compounds which have been prepared: *α-naphthylamine trinitrobenzene*, m. p. 214°; *β-naphthylamine trinitrobenzene*, m. p. 162°; *α-naphthylamine trinitrotoluene*, m. p. 141·5°, the *β-isomeride*, m. p. 113·5°; *α-naphthylamine picramide*, m. p. 203°, and the *β-isomeride*, m. p. 161·5°; *α-naphthylamine ethyltrinitrobenzoate*, m. p. 135°, and the *β-isomeride*, m. p. 126°; *α-naphthylamine ethylpicrate*, m. p. 79·5°; and *α-naphthylamine methylpicrate*, m. p. 75°.

With the object of determining the constitution of these compounds, the action of acetic anhydride and of alcoholic potash on them has been studied; it was thought probable that these reagents might indicate the presence of a hydroxyl group.

α-Naphthylamine trinitrobenzene and acetic anhydride warmed for a few minutes yield a monoacetyl derivative, which crystallises from benzene in sulphur-yellow needles melting at 140·5°. The compound has the acetyl group attached to nitrogen, as the same substance may be obtained by the direct union of trinitrobenzene and α-acetnaphthalide, and as it yields α-acetnaphthalide on treatment with methyl alcoholic potash. Several similar acetyl derivatives have been prepared.

A methyl alcoholic solution of potassium hydroxide decomposes the red compounds, yielding the potassium derivative of trinitrobenzene described by Lobry de Bruyn.

***31. "Acetylation of arylamines." By J. J. Sudborough.**

According to Ulffers and von Janson (*Ber.*, 1894, 27, 93), acid ortho-substituents retard the introduction of an acetyl group into a primary arylamine, but at the same time facilitate the introduction of a second acetyl group. Quantitative experiments have been made by boiling aniline, *o*-toluidine, *p*-toluidine, pseudocumidine, α- and β-naphthylamines with acetic anhydride for an hour and determining the percentage of the arylamine converted into mono- or di-acetyl compounds. The results indicate that a methyl or phenylene group in an ortho-position facilitates diacetylation. All *o*-substituents, whether of a positive or negative character, thus appear to have the property of accelerating the formation of diacetyl derivatives of primary arylamines.

The following new compounds were described: *Diacetyl-pseudocumidine*, $C_6H_2Me_3{\cdot}NAc_2$ [$Me_3 : N = 1 : 2 : 4 : 5$], well developed, transparent prisms melting at 69·5°; *diacetyl-α-naphthylamine*, $C_{10}H_7NAc_2$, colourless, hard prisms melting at 130°; *diacetyl-β-naphthylamine*, colourless plates melting at 66·5°; and *diacetyl-2 : 6-dibromaniline*, large prisms melting at 100°. Most of these diacetyl derivatives crystallise remarkably well, and are readily soluble in the ordinary organic solvents.

***32. "Formation of amides from aldehydes." By R. H. Pickard and W. Carter.**

When an aldehyde is oxidised with ammonium persulphate in the presence of lime, a 30—40 per cent. yield of the amide of the corresponding acid is obtained. The greater portion of the remainder of the aldehyde can be recovered unchanged, and by further oxidation the yield of amide can be increased to 70 per cent. of the weight of aldehyde taken. Substituted amides can be obtained by using potassium persulphate and an amine.

***33. "A method of isolating maltose when mixed with glucose." By A. C. Hill, M.A.**

This method is, essentially, one of removal of the glucose by fermentation with *Saccharomyces Marxianus*, a yeast observed by Hansen in 1888 as not fermenting maltose. It includes also certain details of procedure, which have been found to facilitate, even if they are not necessary to, an easy crystallisation of the maltose after the fermentation is over, and reduce to a minimum such adventitious impurities as

the bye-products of fermentation and the oxidation products of the sugars.

A pure culture of the yeast, which has been grown in a glucose broth, is washed repeatedly with sterilised tap water, making use of a centrifuge, and is then added to a sterilised solution of the sugars which it is desired to ferment. The solution, which may be in an ordinary flask closed by a cotton wool plug, should not contain much more than 10 per cent. of sugar and should be made up in part with sterilised tap water.

The fermentation is conducted at 25—29° and proceeds slowly in the absence of proteid and without any notable multiplication of the yeast cells. When the evolution of carbon dioxide has nearly ceased, the flask is heated for a minute or so at 100° in the autoclave, and then its contents are freed from cells by filtration through a porous funnel. Alcohol is added to the solution to one-third of its volume and the whole evaporated down in a current of carbon dioxide to a thick syrup under diminished pressure; if necessary, more alcohol is added during the evaporation so that the temperature does not rise above 60°. The rest of the process resembles that usually employed in the recrystallisation of maltose from 80 to 85 per cent. ethyl alcohol and results in the separation of the maltose quite white at the first crystallisation.

***34. "The vapour pressure of aqueous ammonia solution." By E. P. Perman, D.Sc.**

The vapour pressure of aqueous ammonia solutions of concentrations varying from nothing to 35 per cent. has been found by a statical method; the temperatures ranged from 0° to 60°. The curves showing the variation of pressure with concentration at various temperatures are found to be approximately represented by the equation $p(100-c)=ac+bc^2$; a and b are constants, c is the concentration of the ammonia in the solution.

The equation may be put in the form $p(100-c)=c.k$, when $k=a+bc$ and is the reciprocal of the solubility coefficient. The variation of pressure with temperature (the concentration remaining constant) is expressed with fair accuracy by the equation $\log.p=\alpha+\beta t+\gamma t^2$, α, β, and γ being constants, of which γ is always negative.

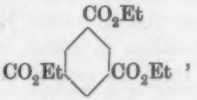
The constant β is found to have the same value as the corresponding constant found in the expression $\log.b=\alpha'+\beta' t$ for the *rate of escape* of ammonia from aqueous solution (*Trans.*, 1898, 73, 511).

***35. "The influence of sodium sulphate on the vapour pressure of aqueous ammonia solution." By E. P. Perman, D.Sc.**

The author has determined the vapour pressures of ammonia solutions containing sodium sulphate in solution at temperatures varying from 26° to 47° and has compared them with corresponding solutions of ammonia without sodium sulphate. The curves show no break at 33°, nor do they diverge more than those for ammonia solution. Hence it seems probable that the sodium sulphate does not exist as a hydrate in solution.

36. "Formation of aromatic compounds from ethyl glutaconate and its derivatives. The reduction of trimesic acid and the conversion of tetrahydrotrimesic acid into tetrahydroisophthalic acid." By W. T. Lawrence and W. H. Perkin, jun.

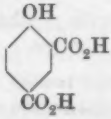
In experimenting with the sodium compound of ethyl sodio-dicarboxyglutaconate, $(CO_2Et)_2CNa{\cdot}CH{:}C(CO_2Et)_2$, the authors have found that this compound, when heated with alcohol at 150°, is decomposed with formation of a large yield of *ethyl trimesate*,



and further, that methyl sodiodicarboxyglutaconate under the same conditions is converted into *methyl trimesate*.

When the sodium compound of ethyl glutaconate, $CO_2Et{\cdot}CHNa{\cdot}CH{:}CH{\cdot}CO_2Et$, is heated with alcohol at 150°, it is also decomposed, but in a different manner, and the product on hydrolysis yields *hydroxyisophthalic acid*.

This acid was identified by analysis, and by conversion into the methyl ester (m. p. 94°) and into the ethyl ester (m. p. 52°), and it is thus identical with the hydroxy*iso*phthalic acid,

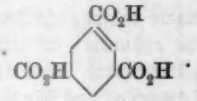


which Kupferberg (*J. prakt. Chem.*, 1877, [ii], 16, 428) obtained by heating sodium salicylate in a current of carbon dioxide.

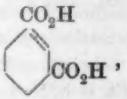
When ethyl methylglutaconate, $CO_2Et{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO_2Et$, is heated with sodium ethylate and alcohol at 140°, it yields a solid ester melting at 96° which, on hydrolysis, is converted into an acid

very sparingly soluble in water and melting at 216°; these substances are at present under investigation. The authors have also found that when the sodium compound of ethyl malonate is digested with ethyl trichloroacetate there is formed, besides the sodium compound of ethyl dicarboxyglutaconate (Ruhemann, *Ber.*, 1896, **29**, 1017), an ester which on hydrolysis and elimination of carbon dioxide, yields aconitic acid. This ester, which is the normal product of the reaction, therefore must have the formula $(CO_2Et)_2CH\cdot C(CO_2Et):C(CO_2Et)_2$.

When trimesic acid, dissolved in sodium carbonate, is treated with sodium amalgam, it is readily reduced with formation of a mixture of acids, which are evidently stereoisomeric modifications of tetrahydrotrimesic acid,



One of these acids has been isolated in a pure condition, it melts at about 210° and is very sparingly soluble in dry ether. When digested with acetic anhydride it yields a resinous double anhydride of trimesic acid and acetic acid, which on distillation loses carbon dioxide, with formation of the anhydride of tetrahydro*iso*phthalic acid. On treatment with potash this anhydride yields tetrahydro*iso*phthalic acid as a colourless crystalline substance sparingly soluble in water and melting at 244°; from its method of formation it must have the formula,



and is the first tetrahydro*iso*phthalic acid which has so far been prepared. The authors are continuing their investigation on the action of sodium ethylate on the derivatives of glutaconic acid and other similarly constituted acids.

37. "Optical activity of certain ethers and esters." By P. A. Guye.

The author has confirmed the results of Tschugaeff's observations, quoted by McCrae and Patterson (Trans., 1900, **77**, 1096) that the optical rotation of compounds containing the phenacetyl group resembles more closely that of compounds containing the acetyl or the chloroacetyl group, than that of compounds containing the toluyl group, although the mass of the phenacetyl group is more nearly that of the toluyl group than of either of the other groups named. The

examination of a number of compounds of amyl (phenyl-amyl oxide· benzyl-amyl oxide, and various amyl esters) has led the author to an analogous conclusion. It is, however, only one case of a more general conclusion already drawn by him, namely, that when substitutions of chains or groups of elements are effected in an asymmetric carbon compound, sufficiently far from the asymmetric carbon atom, the optical rotation is only slightly affected.

38. "Halogen-substituted thiosinamines." By A. E. Dixon, M.D.

From the researches of Gabriel and others, as well as from his own previous work, the author thought it not unlikely that the 'chlorallylthiourea' of Henry (*Ber.*, 5, 188), obtained from β-chloroallylthiocarbimide and ammonia, might really be the hydrochloride of a ring-compound, $CH_2{:}C\!\!<\!\!\begin{matrix}S\\ CH_2\cdot N\end{matrix}\!\!>\!C\cdot NH_2$; to test this, he has prepared the thiocarbimide, and examined a number of its compounds with bases.

Contrary to anticipation, the addition products so obtained are not closed chain saline derivatives; no formation of haloid acid occurs, but the constituents unite directly, yielding the corresponding halogen-substituted thiocarbamides.

β-Chloroallylthiocarbimide, $CH_2{:}CCl\cdot CH_2\cdot NCS$, is a colourless, highly refracting oil boiling at about 182°; it is slightly soluble in water, has a very pungent odour, and readily blisters the skin.

With ammonia it yields Henry's β-chloroallylthiourea; prisms, melting at 93·5—94·5° (corr.); Henry gives 90—91°. This substance is moderately soluble in water, and easily so in alcohol; the latter solution, if moderately dilute, gives no precipitate with silver nitrate, but is freely desulphurised by warming with alkaline lead tartrate. Chloroallylthiourea undergoes no isomeric change if boiled in aqueous solution; when fused with monochloracetic acid, it yields the hydrochloride of *β-chloroallylthiohydantoin*, $CH_2{:}CCl\cdot CH_2\cdot NH\cdot C\!<\!\!\begin{matrix}S-CH_2\\ N\cdot CO\end{matrix}$, white prisms, which begin to decompose at about 170°, and lose the combined acid on recrystallisation from water. The free thiohydantoin is deposited from water in leaves, and from alcohol in prisms, both forms melting at 149°; when hydrolysed by boiling with dilute alkali, thioglycollic acid is produced.

ab-*Chloroallylphenylthiocarbamide*, $CH_2{:}CCl\cdot CH_2\cdot NH\cdot CS\cdot NH\cdot C_6H_5$, prepared from the thiocarbimide and aniline, is deposited from benzene in plates, m. p. 91—92°. When desulphurised by silver nitrate it gives rise to the corresponding ab-*chloroallylphenylcarbamide*, as slender prisms, m. p. 151—152°.

ab-*Chloroallylorthotolylthiocarbamide* separates from weak alcohol in prisms, m. p. 84—85°.

ab-*Chloroallylbenzylthiocarbamide* crystallises from a mixture of benzene and light petroleum in very brilliant prisms, m. p. 69°. Unlike the preceding thiocarbamides, it is not desulphurised when boiled with alkaline lead tartrate.

Piperidine yields *chloroallylpiperidylthiourea* in transparent quadrangular plates, m. p. 146·5—147·5°.

n-*Chloroallyl-v-benzylphenylthiourea*, $C_3H_4Cl{\cdot}N{:}C(SH){\cdot}NBzPh$, is deposited from light petroleum in needles, m. p. 77—78°.

β-Chloroallylthiocarbimide, dissolved in chloroform, absorbs bromine, yielding *β-chloro-βγ-dibromopropylthiocarbimide*,

$$CH_2Br{\cdot}CClBr{\cdot}CH_2{\cdot}NCS,$$

a dense, yellowish liquid, volatile in a current of steam; it unites spontaneously with aniline, forming the hydrobromide of a ring compound, $C_3H_4BrCl{<}\overset{N}{S}{>}C{\cdot}NH{\cdot}C_6H_5$. The hydrobromide occurred as a sandy powder, m. p. 112—113°; when treated with cold alkali, hydrogen bromide was removed, but the base could not be obtained in a state fit for analysis.

With benzylamine an oily hydrobromide was produced; from this potash withdraws a molecule of hydrogen bromide, leaving the free base, $C_3H_4Br_2{<}\overset{N}{S}{>}C{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$, which crystallises in prisms, m. p. 107—108°, and dissolves in hydrobromic acid to re-form the oily hydrobromide.

39. "A form of tautomerism occurring amongst the thiocyanates of electro-negative radicles." By A. E. Dixon, M.D.

Some years ago (*Trans.*, 1897, 71, 640; see also 1899, **75**, 389), the author remarked that the so-called "phosphorus trithiocyanate," $P(SCN)_3$, appeared to possess thiocarbimidic as well as thiocyanic properties, and subsequent investigation tends to show that this power to function in both capacities is also manifested by the products obtainable from metallic thiocyanates and the chlorides of a number of electro-negative mineral elements and compound radicles.

The chlorides, dissolved in suitable anhydrous solvents, were caused to interact with excess of lead or other metallic thiocyanate, if possible, until the chlorine was completely eliminated as metallic chloride; the solid residue was then filtered off, and the filtrate treated with a base such as aniline. Precipitates were thus obtained, which gave the desulphurisation tests with lead and silver salts, characteristic of thiocarbamides, and were usually hydrolysed by contact with water so as to afford the substituted thiourea corresponding to the base used.

Unfortunately, no efficient method has yet been found for purifying these precipitates, which are rarely free from more or less contamination with basic thiocyanate.

"Phosphorus trithiocyanate," $P(SCN)_3$, gave with aniline a yellow solid insoluble in cold water, but decomposed when boiled with water into phenylthiourea and an acid of phosphorus; this substance is probably phosphorus triphenyltrithiourea, $P(NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5)_3$. With *o*-toluidine a yellow powder melting between 81° and 83° was obtained; it appears to be the corresponding tolyl derivative nearly pure. Both these compounds are very freely soluble in alcohol and acetone, but nearly insoluble in benzene, chloroform, and light petroleum.

"Phosphoryl trithiocyanate," $PO(SCN)_3$, obtained in solution by boiling phosphorus oxychloride in dry cumene with lead thiocyanate, gave with silver and lead salts the usual thiocarbimidic reactions; and united spontaneously with aniline, *o*-toluidine and dry ammonia.

The *aniline* compound was a pale yellow powder melting at about 111—112°, freely soluble in alcohol, ethyl acetate, acetone, glacial acetic acid, and nitrobenzene; insoluble, or nearly so, in chloroform, ether, carbon disulphide, benzene and light petroleum. It was nearly insoluble in cold water, but dissolved gradually on boiling; the solution contained phosphoric and thiocyanic acids, and on cooling, gave a crystalline deposit of phenylthiourea. The latter appears to be formed by hydrolysis of phosphoryltriphenyltrithiocarbamide: $PO(NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5)_3 + 3H_2O = H_3PO_4 + 3CSN_2H_3{\cdot}C_6H_5$.

Orthotoluidine gave a tenacious oil, hardening presently to a resin-like solid; its properties resembled those of the phenylic homologue but the substance could not be obtained in a pure condition.

Dry *ammonia* gas yielded a pale yellow granular solid, melting, imperfectly, below 60°, readily soluble in water, and containing a very appreciable quantity of ammonium thiocyanate. The solution in cold water gave with excess of ammonia, followed by magnesia mixture, scarcely any precipitate. But this solution, if previously boiled and allowed to cool, then reacted freely with the above test; consequently it is inferred that the phosphoric acid does not exist ready formed in the solution, but originates through the hydrolysis of the phosphoryltrithiourea, $PO(CSN_2H_3)_3$.

The "thionyl thiocyanate" of McMurtry (*Trans.*, 1889, **55**, 48) differs in physical and chemical characters from all the known electronegative thiocyanates; it is suggested that this compound, of which the thiocyanic properties are very feebly marked, whilst it gives decided thiocarbimidic reactions, is probably a polymeric form, $[SO(NCS)_2]_n$.

Carbonyl chloride, in toluene, reacted with lead thiocyanate on standing; the dissolved sulphuretted product (which was freely de-

sulphurised by lead and silver salts) combined at once with aniline, yielding in small quantity a substance melting at about 174° and possessing the characters of a thiocarbamide.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Whitehall Rooms, Hotel Metropole, on Wednesday, March 27th, at half-past six for seven o'clock.

The price of the tickets is one guinea each including wine.

Fellows are particularly requested to give the Secretaries early notice of their intention to be present.

Tickets will be forwarded to Fellows on receipt of a remittance for the number of tickets required, addressed to the Assistant Secretary, Chemical Society, Burlington House, W.

ANNUAL GENERAL MEETING.

The Annual General Meeting of the Society for the Election of Officers and other business will be held on Thursday, March 28th, at three o'clock in the afternoon.

At the next meeting, on Thursday, March 21st, the following papers will be communicated:

"Researches on morphine. Part II." By S. B. Schryver and F. H. Lees.

"The constitution of pilocarpine. Part II." By H. A. D. Jowett.

"Note on the latent heats of evaporation of liquids." By H. Crompton.

"Action of dry silver oxide and ethyl iodide on benzoylacetic ester, desoxybenzoin, and benzyl cyanide." By G. D. Lander.

"Alkylation of acylarylamines." By G. D. Lander.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 235.

March 21st, 1901. Professor THORPE, C.B., F.R.S., President, in the Chair.

Messrs. G. D. Lander, H. W. Kinnersley, and E. F. Linstead were formally admitted Fellows of the Society.

The following certificates were read for the first time:—William Henry Duckworth, 87, New Bank Road, Blackburn; Samuel Philip Eastick, 25, Woodville Road, Ealing; Ernest Alfred Lewis, 310, Dudley Road, Birmingham; Alexander McKenzie, Jenner Institute, S.W.; Edgar Neuman, 10, Randolph Crescent, Maida Vale, London; William Oldershaw, Market Place, Nottingham; Samuel Siefrig, 18, Waterloo Road, Shepton Mallet, Som.; James Smith, 14, Mersey Road, Aigburth, Liverpool.

REPLY TO THE ADDRESS TO THE KING.

The SECRETARY read the following reply which His Majesty the King has been graciously pleased to cause to be made to the Address of the President, Council, and Fellows of the Society.

MARLBOROUGH HOUSE,
PALL MALL, S.W.
23rd February, 1901.

The Private Secretary is commanded by the King to thank the President, Council, and Fellows of the Chemical Society, for the kind expression of their sympathy with His Majesty, on the occasion of the lamented death of Her late Majesty the Queen, and for the loyal and dutiful sentiments conveyed in their Address to the King.

DAY AND HOUR OF MEETING.

The following is the report of the Committee appointed by the Council to examine the cards returned by Fellows in reply to the question as to the suggested change in the Day and Hour of the Ordinary Meetings to Wednesday, at 5.30 p.m. :—

"Nineteen hundred cards were issued to Fellows, and 1000 answers were returned. Of these, 581 were unreservedly in favour of the change, namely, 256 London Fellows, and 325 Country Fellows. 118 Fellows, whilst not voting unreservedly for the change, said they offered no objection to it. 172 Fellows were unreservedly opposed to the change. Of the 129 Fellows remaining, 85 expressed no objection to the change of day, but offered suggestions as to change of hour. 3 suggested meeting at 3, 1 at 4, 1 at 4.30, 12 at 5, 12 at 6, 9 at 6.30, 10 at 7, 5 at 7.30, 15 at 8, and 2 at 8.30. 11 suggested a later hour than 5.30 without particularising it, and 4 alternately 5 30 and 8. 24 Fellows suggested meeting on some other day than Wednesday or Thursday, namely, 2 on Monday at 5.30, 1 on Tuesday at 8, 14 on Friday, 10 of whom preferred 5.30; of the remaining 4, 2 indicated no preference as to hour, 1 suggested 8, and 1 suggested 8.30. 7 Fellows suggested various hours on Saturday afternoon or evening. 16 Fellows preferred Thursday, but suggested some other hour than 8, 11 suggested 5.30, 1 preferred 6, and 3 preferred 7. 1 suggested 8.30. 4 Fellows deprecated the change on the ground that it clashed with the present arrangements of the Society of Public Analysts.

"Analysing the replies of those Fellows who have contributed papers to the Society, 266 of whom have responded, 188 have voted for the change, and 78 against it."

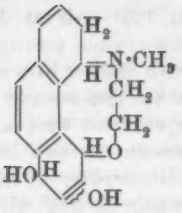
Of the following papers, those marked * were read:

*40. "Researches on Morphine. Part II." By S. B. Schryver and F. H. Lees.

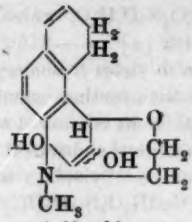
The authors have shown (*Trans.*, 1900, **77**, 1024) that bromomorphide, $C_{17}H_{18}O_2NBr$, is decomposed by water in accordance with the equation $C_{17}H_{18}O_2NBr + H_2O = C_{17}H_{19}O_3N,HBr$, and from the reaction product a new base, isomeric with morphine and designated *isomorphine*, was isolated and described. The authors have since isolated from the product of the above reaction another new base, *β*-iso*morphine*, $C_{17}H_{19}O_3N$, which is formed only in relatively small amount. It crystallises from alcohol in double pyramids of the formula

$2C_{17}H_{19}O_3N,C_2H_6O$, which, after drying at 120° melt at 182°, and for which $[\alpha]_D^{17} = -216{\cdot}2°$. Chloromorphide, when decomposed by water, also yields *β-iso*morphine, together with another base which has not yet been further examined. In view of the non-narcotic action of *iso*morphine as compared with morphine, experiments were carried out to determine the chemical relationship between the two isomerides. *iso*Morphine yields a *diacetyl* iso*morphine methiodide*, $C_{17}H_{17}(O{\cdot}CH_3CO)_2ONCH_3I$, as needles melting at 242° with decomposition. Phosphorus tribromide reacts with *iso*morphine, giving bromomorphide (*m.* p. 170°) identical with that obtained from morphine by the same reaction. Phosphorus trichloride, on the other hand, reacts with *iso*morphine, yielding no definite product, whereas chloromorphide results from the same reaction with morphine. iso*Codeine methiodide*, $C_{17}H_{18}O_2(OCH_3)NCH_3I$, forms leaflets melting at 265° with decomposition, and for it $[\alpha]_D^{17} = -102{\cdot}1°$. It was prepared by the three following methods: (*a*) by the action of silver sulphate and barium hydroxide on *iso*morphine methiodide, with subsequent interaction of the resulting methydroxide and methyl iodide; (*b*) by the action of excess of methyl iodide on the sodium derivative of *iso*morphine; (*c*) from codeine by the following steps: *bromocodeide*, $C_{17}H_{17}O(OCH_3)N{\cdot}Br$, prepared by the action of phosphorus tribromide on codeine, forms pearly scales melting at 162°, for which $[\alpha]_D^{20} = +56{\cdot}7°$; iso*codeine*, $C_{17}H_{18}O_2(OCH_3)N$, from the action of water on bromocodeide, which forms needles melting at 144°, for which $[\alpha]_D^{15} = -169°$. The methiodide was then readily prepared from *iso*codeine.

The formation of *iso*codeine methiodide by the above methods confirms the phenolbetaine constitution, $C_{16}H_{15}O_2{<}^{O}_{N(CH_3)_2}$, for *iso*morphine methydroxide, which was provisionally assigned to this substance by the authors in their previous paper. Sodium hydroxide reacts with *iso*codeine methiodide, yielding the base *methi*-iso*morphimethin*, $C_{16}H_{14}O_2(OCH_3){\cdot}N(CH_3)_2$, which forms tables melting at 167°, and having $[\alpha]_D^{20} = +64{\cdot}6°$. *Methi*-iso*morphimethin methiodide*, $C_{16}H_{14}O_2(OCH_3){\cdot}N(CH_3)_2I$, forms needles melting at 265°, and for which $[\alpha]_D^{17} = +34{\cdot}7°$. *Methi*-iso*morphimethin methydroxide* is split up by the action of heat and yields morphenol methyl ether, $C_{15}H_{10}O_2$, m. p. 65°, which is identical with the phenol obtained by Knorr (*Ber.*, 1889, **22**, 183) from codeine methiodide, the morphine derivative, by analogous reactions to the above. These results indicate the presence in *iso*morphine of exactly the same groups as occur in morphine, and the authors suggest that the relationship between these two bases is, in all probability, similar to that represented by the two following formulæ:



Morphine (Knorr).



*iso*Morphine.

The different physiological behaviour of morphine and *iso*morphine was treated of from the standpoint of Ehrlich's view.

***41. "The constitution of pilocarpine. Part II." By H. A. D. Jowett, D.Sc.**

When bromine acts on *iso*pilocarpine in acetic acid solution, dibromo*iso*pilocarpine perbromide is formed as the chief product of the reaction, but small quantities of monobromo*iso*pilocarpine and *iso*pilocarpinic acid are also produced. *Dibromoisopilocarpine perbromide*, $C_{11}H_{14}O_2N_2Br_2 \cdot HBr_3$, crystallises in needles melting at 165°. Treated with ammonia, *dibromoisopilocarpine*, $C_{11}H_{14}O_2N_2Br_2$, is formed, crystallising in rectangular prisms melting at 135°. It is optically inactive and is only feebly basic, being precipitated from its solution in strong acids by water; it does not react with methyl iodide. On reduction, it is converted into *iso*pilocarpine. *Monobromoisopilocarpine*, $C_{11}H_{15}O_2N_2Br$, forms needles melting at 164°. Isopilocarpinic acid, $C_{11}H_{16}O_4N_2$, was only obtained as an oil. It yields a microcrystalline barium salt, $(C_{11}H_{15}O_4N_2)_2Ba$, and is therefore monobasic.

Dibromo*iso*pilocarpine, on oxidation with permanganate, yields hydrobromic acid, ammonia, methylamine, a new acid termed *pilopinic acid*, $C_8H_{11}O_4N$, and the acid, $C_7H_{10}O_4$, previously described, and which is now called pilopic acid.

Pilopinic acid, $C_8H_{11}O_4N$, is crystallised with difficulty, forming pearly plates melting at 98°. It is lævorotatory $[\alpha]_D = -13{\cdot}6°$. It is a monobasic lactonic acid. The monoethyl ester boils at 262° at 10 mm. On oxidation it yields ammonia and pilopic acid.

When bromine acts on *iso*pilocarpine in aqueous solution at 100° in a sealed tube, the following products are formed: dibromo*iso*pilocarpinic, monobromo*iso*pilocarpinic, bromopilopinic, and bromopilopic acids, ammonia and methylamine, the two first-named acids being the chief products formed in about equal quantities.

Dibromoisopilocarpinic acid, $C_{11}H_{14}O_4N_2Br_2$, forms rectangular crystals melting at 235°. The acid is dextrorotatory $[\alpha]_D = +24{\cdot}4°$ and is monobasic.

Monobromoisopilocarpinic acid, $C_{11}H_{15}O_4N_2Br$, has only been obtained as a syrup.

When dibromo*iso*pilocarpinic acid is treated with sodium amalgam in alcoholic solution, pilopic acid is formed. This acid, previously described as an oil, has now been obtained in crystals melting at 103°. Both mono- and dibromo-*iso*pilocarpinic acids, on reduction with zinc and glacial acetic acid, yield a new crystalline lactone, *isopilocarpinolactone*, $C_{11}H_{14}O_4N_2,H_2O$, which forms rectangular prisms which melt at 83°. It is lævorotatory, $[\alpha]_D = -51{\cdot}9°$, and is a neutral substance which reacts with strong alkalis, forming salts of hydroxy*iso*pilocarpinic acid, $C_{11}H_{16}O_5N_2$, which are stable. It does not unite with methyl iodide, even when heated in alcoholic solution at 100°.

Dibromopilocarpine, $C_{11}H_{14}O_2N_2Br_2$, first prepared by Pinner and Kohlhammer (*Ber.*, 1900, **33**, 1424), has been further studied; it melts at 95° when pure, and not at 79° as stated by these authors. It is dextrorotatory $[\alpha]_D = +43{\cdot}6°$, and, like its isomeride dibromo*iso*pilocarpine, is very feebly basic and does not unite with methyl iodide. On reduction, it is converted quantitatively into pilocarpine.

Efforts to prepare bromocarpinic acid, first described by the above authors, have been unsuccessful, and results have been obtained which indicate that the first action of bromine on pilocarpine at 100° under pressure is analogous to that on *iso*pilocarpine. The bromopilocarpinic acids on reduction, however, yield pilocarpinic acid, $C_{11}H_{16}O_4N_2$, thus differing from the bromo*iso*pilocarpinic acids.

Experiments on the oxidation and attempted reduction of *iso*pilocarpine were also described.

***42. "The chemical action of Bacillus coli communis and similar organisms on carbohydrates and allied compounds." By A. Harden.**

Bacillus coli communis ferments glucose with production of a quantity of lactic acid corresponding to rather less than half the sugar, and of alcohol and acetic acid in approximately equivalent amounts, each representing about one-sixth of the carbon of the sugar. Small amounts of succinic and formic acids are also produced and carbon dioxide and hydrogen evolved. The carbon dioxide amounts to 12—18 per cent. of the sugar, whilst the volume of hydrogen is slightly greater. The lactic acid formed was found to be a mixture of inactive acid (25—5 per cent.) with *l*-lactic acid (75—95 per cent.). *B. typhosus* produces the same products from glucose, except that it yields a large amount of formic acid (17 per cent.) and no gas. Some of the abnormal forms of *B. coli communis* act in a similar manner on glucose, others produce the same substances but in entirely different proportions. *d*-Fructose

yields the same products of fermentation by *B. coli communis* as glucose, and *l*-arabinose and *d*-galactose also yield *l*-lactic acid. Mannitol yields a much larger proportion of alcohol, 26—29 per cent., and a much smaller amount of lactic and acetic acids. The production of alcohol by this organism therefore appears to depend on the presence of the group $CH_2(OH)\cdot CH\cdot OH$ in the compound to be fermented; glycerol, which also contains this group, yields nearly half its weight of alcohol when fermented by the same organism.

Formic acid is decomposed into carbon dioxide and hydrogen (Pakes and Jollyman), but lactic acid is not attacked and hence the active lactic acid is probably not produced by the selective decomposition of previously formed inactive acid.

When asparaginic acid is the sole nitrogenous nourishment, glucose and mannitol are fermented as usual by this organism, but a large proportion of the hydrogen is absorbed and reduces the asparaginic acid to ammonium succinate.

Discussion.

Mr. Pakes remarked with regard to the fact that Dr. Harden's experiments were made under anaerobic conditions, that quite different decompositions took place when the conditions were altered; for example, when nitrates were present with *d*-glucose, nitrogen was evolved instead of hydrogen; the yield of lactic and acetic acids was quite altered if the medium containing *d*-glucose had abundant oxygen either free or in the form of nitrates. Again, out of 84 strains of typical *B. coli communis* under observation at the present time, about two-thirds inverted sucrose and subsequently fermented it, the remainder, failing to invert it, did not ferment it; a similar selective power was noticed in the case of glycerin. Some, again, did not appear to be able to start the fermentation of glycerin under anaerobic conditions, but if the process were started, it would then continue anaerobically. He had observed a similar reaction with the *B. fluorescens liquefaciens* in media containing nitrates; the bacillus would not begin to grow in this medium under anaerobic conditions, but if the growth were started by the introduction of a few cubic centimetres of oxygen, the decomposition of the nitrate would continue under strictly anaerobic conditions.

Dr. Harden, in reply, stated that the products of fermentation, in the presence and absence of oxygen, had frequently been found to be different. Anaerobic conditions seemed likely to furnish the most interesting results. The reduction of nitrates by this organism in presence of glucose appeared to be a secondary reaction of the same order as the reduction of asparaginic acid. The variability

of the action of the organism on cane sugar had been previously observed by Cushing, who, however, had not investigated the interesting question as to the inversion of the sugar by this organism.

***43. "Action of dry silver oxide and ethyl iodide on benzoylacetic ester, deoxybenzoin, and benzyl cyanide." By G. D. Lander, D.Sc.**

The author has studied the action of silver oxide and ethyl iodide on benzoylacetic ester, deoxybenzoin and benzyl cyanide, as further examples of compounds analogous to acetoacetic ester (*Trans.*, 1900, 77, 729).

With benzoylacetic ester either at the temperature of the steam-bath or in the cold, the course of the reaction is entirely similar to that of acetoacetic ester, the alkylated product consisting almost entirely of C-ethyl homologue, mixed, however, with minute quantities of β-ethoxycinnamic ester (Claisen, *Ber.*, 1896, 29, 1006). These substances were identified by dilute alkali hydrolysis, when phenyl propyl ketone, giving an oxime, m. p. 55—56° ($N = 8{\cdot}94$ instead of 8·59 per cent.), was obtained. The alkaline hydrolysis liquid yielded small quantities of β-ethoxycinnamic acid, separating by slow crystallisation from dilute alcohol in prisms, by more rapid recrystallisation in leaflets melting at 160·5° with energetic evolution of gas, Claisen (*loc. cit.*) gives m. p. 162°; the isomeric ethylbenzoylacetic acid melts at 116°.

Only oxidation products were obtained from deoxybenzoin and benzyl cyanide.

After boiling deoxybenzoin for 8 hours with silver oxide and ethyl iodide an unchanged substance and a minute quantity of a compound (m. p. 245°) sparingly soluble in alcohol alone resulted. This latter compound was evidently bidesyl (m. p. 255°).

By the action of silver oxide on benzyl cyanide, either in the presence of ethyl iodide on the steam-bath, or in the absence of iodide in the cold, profound decomposition ensued. By rapidly heating the thick tarry product in a vacuum small distillates of dicyanostilbene were obtained (m. p. 158—159°), which gave the characteristic fluorescent green prisms of diphenylmaleic anhydride (m. p. 155°) on hydrolysis with alcoholic potash.

***44. "Alkylation of Acylarylamines." By G. D. Lander, D.Sc.**

The alkylation of various acylarylamines, containing the aceto-, benzo-, oxalyl-, and oxal-residues, by means of dry silver oxide and alkyl iodides has been studied.

By means of oxide and ethyl iodide, O- or imino-ethers alone result, whereas when methyl iodide is employed the alkylation usually gives

a mixture of N- or acylalkylamine, and O- or imino-homologues. Apparently the methylation of acet-*p*-toluide yields N-ether alone. A partial explanation of this anomalous action of methyl iodide is afforded by the observation that simple heating serves to convert N-phenylacetiminomethyl ether, $C_6H_5N\ C(OCH_3)CH_3$, into the N-substituted isomer.

The imino-ethers corresponding to acylarylamines are readily distinguished from the isomeric N-substituted compounds; by their liquidity at the ordinary temperature; by their boiling points, which are from 30—50° lower than those of the acylalkylamines; by the characteristic behaviour on heating of their hydrochlorides (when obtainable), regenerating acylarylamine by loss of alkyl chloride, and by their very ready hydrolysis by dilute hydrochloric acid into the original amine, acid and alcohol. The presence of a methyl group in the ortho-position in the N-*o*-tolyl imino-ethers, however, inhibits this characteristic hydrolysis, it being possible to prepare platinichlorides of these ethers from aqueous solutions. N-α-Naphthylacetimino-ethyl ether seems also to possess greater relative stability than the β-naphthylisomer.

The following compounds have been obtained: From acetylarylamines: N-*phenylacetiminomethyl ether* (with N-isomer), b. p. 197°; N-*o-tolylacetiminoethyl ether*, b. p. 222°, *hydrochloride*, m. p. 90—91° (with regeneration of acetotoluide), *platinichloride*, m. p. 171°; N-*o-tolylacetiminomethyl ether* (along with N-isomer), b. p. 212° (atmos.), *hydrochloride*, m. p. 79—80°, *platinichloride*, m. p. 169°; N-*p-tolylacetiminoethyl ether*, b. p. 232° (hydrochloride unstable); N-*α-naphthylacetiminoethyl ether*, b. p. 175° (12 mm.), *hydrochloride*, m. p. 111°; N-*β-naphthylacetiminoethyl ether*, b. p. 176·5° (12 mm.). From benzanilide; N-*phenylbenziminoethyl ether*, formerly prepared by Lossen (*Ann.*, 1891, **265**, 138), b. p. 176° (12 mm.). From oxanilic ester, *semi*-N-*phenylimino-oxalic diethyl ether*, $C_6H_5N{:}C(OC_2H_5)\cdot CO_2C_2H_5$. The dimethyl ether has been described by Anschütz and Stiepel (*Ber.*, 1895, **28**, 61). The diethyl ether is a liquid, b. p. 152—155° (12 mm.), decomposed by dry hydrochloric acid apparently into a mixture of oxanilic ester and anhydrous oxanilic acid; with aniline at 100° it gives *diphenylamidino-oxalic ester*, $C_6H_5N{:}C_6H_5NH\cdot C\cdot CO_2C_2H_5$, m. p. 73—74·5°, a base giving a stable platinichloride, and passing by warming with aniline at 160—170° into *diphenylamidino-oxalanilide*, melting when rapidly heating at 140—142°, softening at 134°.
From oxanilide: *di*-N-*phenylimino-oxalic diethyl ether*, $\{C_6H_5N{:}C(OC_2H_5)\}_2$, a viscid, brown, rather unstable oil, b. p. 205° (12 mm.).

***45. "The preparation of aliphatic imino-ethers from amides." By G. D. Lander, D.Sc.**

The synthesis of imino-ethers from acid amides has only been found possible hitherto with certain aromatic amides which give stable silver salts (Tafel and Enoch, *Ber.*, 1890, **23**, 103). The same authors, in a later paper (*loc. cit.*, 1550), describe unsuccessful attempts to effect the analogous synthesis from some aliphatic amides.

The author has examined the possibility of accomplishing this by the aid of dry silver oxide and ethyl iodide.

Semi-imino-oxalic diethyl ether, $NH{:}C(OEt)\cdot CO_2Et$ (compare Nef, *Ann.*, 1895, 287, 288), boiling at 75—77° at about 20 mm., can be readily prepared from ethyl oxamate by means of silver oxide and ethyl iodide at 100°. When urethane is warmed with ethyl iodide and silver oxide, there occurs a vigorous reaction, a liquid boiling from 90—200°, along with small quantities of triethyl isocyanurate, m. p. 93—94°, being obtained. The liquid is probably a mixture of ethyl iminocarbonate, unchanged urethane, and triethyl cyanurate.

The formation of imino-carbonic diethyl ether can be demonstrated by carrying out the reaction in the cold, separating the imino-ether from unaltered urethane by distillation below 85° (20 mm.), purification by means of potassium hydroxide and conversion by hypobromite into bromiminocarbonic diethyl ether, m. p. 40—42°, 0·4 gram being thus obtained from 18 grams of urethane.

The results of several experiments with acetamide, silver oxide, and ethyl iodide, carried out either at 100° or in the cold, unfortunately still leave the question of the formation of acetiminoethyl ether by this process open. The production of a liquid base of 'imino' odour, volatile between 70° and 100°, from which, however, so far, only an oily hydrochloride has been prepared, nevertheless inclines the author to suppose that acetiminoethyl ether is actually one of the products of the reaction.

46. "Note on the latent heats of evaporation of liquids." By H. Crompton.

Imagine a saturated vapour in so attenuated a state that the gas law $PV=RT$ applies to it. Assume that it were possible at constant temperature and by compression alone to reduce the volume of the vapour V_0 to the volume which the liquid it forms would normally occupy v_0, *without any change in state occurring, and the substance during this compression continuing to obey the gas law.* The work done in bringing about this change in volume would be

$$\int_{v_0}^{V_0} p dv = \int_{v_0}^{V_0} \frac{RT}{v} dv = RT \log_e V_0/v_0$$

and, as no change in temperature occurs, heat equivalent to this work will be given out during compression.

The vapour now occupies the volume of the liquid, but it is not yet liquid. It is by assumption a gas under high pressure, and if the pressure is now reduced to its original amount, the gas would expand to its original volume. To form the liquid the substance must be brought to such a state that it would be possible to reduce the pressure to the normal vapour pressure of the liquid, without any corresponding change in volume. Assuming that no change in molecular aggregation occurs, the substance must then be deprived of the potential energy of expansion of the gas, that is, of the energy that would enable the molecules of the substance to occupy their original volume on a return to the original pressure. This energy is equal to that expended in compressing the material, namely, $RT\log_e V_0/v_0$. If this is removed in the form of heat, the total heat given out during the production of the liquid from the vapour is $2RT\log_e V_0/v_0$, and this is the latent heat of evaporation.

If, in the above, V_0 and v_0 apply to the gram-molecule, R would have the value 1·976 calories, and $2RT\log_e V_0/v_0$ would be the molecular heat of evaporation. Dividing this by the molecular weight M, the latent heat of evaporation would be obtained in the ordinary units.

The observations of Cailletet and Mathias with carbon dioxide nitrous oxide and sulphur dioxide allow the above formula to be tested for fairly wide variations in temperature and pressure. D_0 is the density of the vapour, d_0 the density of the liquid, l the latent heat of evaporation. The calculated values are obtained by the method described.

	T.	D_0.	d_0.	M.	l obs.	l cal.
Carbon dioxide	248	0·044	1·110	44	72·23	71·91
,, ,,	273	0·099	0·905	44	57·48	54·26
,, ,,	295·04	0·233	0·720	44	31·80	31·06
Nitrous oxide	253	0·044	0·998	44	66·90	70·93
,, ,, ...	273	0·081	0·890	44	59·50	58·77
,, ,, ...	293	0·151	0·755	44	43·25	42·36
Sulphur dioxide	273	0·0045	1·4338	64	91·2	97·17
,, ,,	303	0·0136	1·3520	64	80·5	86·05
,, ,,	335	0·0364	1·2425	64	68·4	70·03

In calculating the latent heats of evaporation at the ordinary boiling points of liquids, we have approximately $V_0/v_0 = 22320Td_0/273M$,

if d_0 is the density of the liquid at its boiling point. In general, the calculated values are found to be about 5 to 10 per cent. higher than the observed. This may be attributed to the fact that the saturated vapour at the boiling point is "not a perfect gas, and has usually a slightly higher density" than that corresponding to the normal molecular weight M. With a few associating liquids, notably the alkyl alcohols, the calculated values are somewhat lower than the observed. Here, in addition to the changes described and accounted for, the production of molecular aggregates occurs on liquefaction, doubtless involving the evolution of heat. Hence the observed latent heat is higher than the calculated by this amount.

From the equation $l = 2RT(\log_e V_0 - \log_e v_0)/M$ we get $Ml/T = 2R(\log_e V_0 - \log_e v_0)$. According to the law of Trouton, Ml/T is approximately constant for liquids at their normal boiling points, and has an average value of about 21. It will be found that for most liquids V_0/v_0 varies from 300 to 400. This gives a value varying from 22·8 to 23·9 for Ml/T. As, strictly speaking, in Trouton's formula M is double the vapour density and not merely the theoretical molecular weight, slight abnormalities in the densities of the saturated vapours may account for the difference. As is well known the boiling points are approximately comparable points in the case of liquids. If liquids were truly comparable at the boiling point the ratio V_0/v_0 would be the same for all liquids at this point. Trouton's law according to the above expression would then hold absolutely.

47. "On the atomic weight of lanthanum and on the error of the 'sulphate method' for the determination of the 'equivalent' of the rare earths." By Bohuslav Brauner and F. Pavlíček.

Lanthanum material was prepared from crude cerite material and purified, first by repeated recrystallisation of the double ammonium nitrate. The nitrate was then further purified by fusion with potassium sodium nitrate, traces of cerium, praseodymium, and yttrium being thus removed, after which the material was further fractionated by this process of fusion. The purest lanthanum nitrate was next subjected to a series of fractional precipitations with potassium hydroxide so that about 7/8 of the earth was precipitated, and the most "positive" fraction contained in the filtrate was converted into the pure oxalate and designated as La 1. In the same way, fractions La 2—La 7 were obtained, La 7 being most "negative" of the series. After this followed the still more negative fractions A1—A6, obtained by fusion with nitre.

For the determination of the atomic weight the oxide (from the oxalate) was converted into the sulphate, and the conditions accom-

panying its formation were carefully investigated. On heating the sulphate to a constant temperature of 450° and repeatedly weighing, a gradual decrease of weight was observed until at last an approximately constant weight was obtained corresponding to an atomic weight of about La = 138. On heating the salt in an atmosphere of ammonium carbonate, further loss of sulphuric acid takes place, and an atomic weight of La = 138·2 (O = 16) was obtained with the purest material (La 1), a number which, owing to the concordant determinations of Brauner, Cleve, and Bettendorff, has hitherto been regarded as the true atomic weight of lanthanum. This number is, however, incorrect, a careful investigation having shown that the sulphate so obtained contains some of Wyrouboff's *acid sulphate*. This acid sulphate is so stable that even at temperatures above 500° some of it remains undecomposed, whilst another part of the sulphate, in the same crucible, may have undergone a partial decomposition into the basic sulphate. An aqueous solution of a sulphate so prepared shows, with ethyl orange as indicator, a strongly acid reaction, whereas the true normal sulphate obtained by repeated recrystallisation is perfectly neutral towards ethyl orange. Every sulphate obtained in this way was therefore dissolved in water, tested with ethyl orange, and a *N*/20 solution of sodium hydroxide added until the red colour of the indicator was converted into the yellow tint shown by the normal neutral lanthanum sulphate solution containing ethyl orange. The error of the atomic weight of lanthanum due to the presence of sulphuric acid in the form of an acid sulphate may amount to − 0·8 of a unit.

All "equivalent" determinations of the rare earths made by the "sulphate method" during the 19th century are vitiated by this error. This error is largest with the most positive lanthanum and diminishes as the basicity of the earth decreases.

After the determination and application of the above correction the single fractions of lanthanum gave the following atomic weights (means of several determinations):

La 1.	La 2.	La 3.	La 4.	La 5.	La 6.	La 7.	A 5+6.
138·78	138·80	138·88	138·97	138·98	139·07	139·10	139·25

The sulphate is very hygroscopic and absorbs moisture during weighing. After excluding this error completely by means of a novel cooling and weighing arrangement, it was found that a correction of +0·2 to +0·3 must be applied to the whole series so that the atomic weight of the most positive fraction becomes La = 139·0.

Lanthanum is a complex of two earth metals consisting, however, chiefly of the true lanthanum with the atomic weight La = 139·0. Gibbs' and Shapleigh's results confirm this, for they found for the *mixture* the atomic weight 139·7.

48. "On the atomic weight of praseodymium." By B. Brauner.

The atomic weight of this element was determined by four methods. (1) By the analysis of the anhydrous sulphate. The oxide of the approximate formula, Pr_4O_7, remaining after strong calcination of the sulphate was analysed by Bunsen's iodometric method and the weight of the pure Pr_2O_3 was determined; this series gave Pr = 140·95. (2) By the analysis of the oxalate. The amount of pure Pr_2O_3 contained in the oxide Pr_4O_7, which remains after calcination was determined as in (1) and the oxalic radicle was determined by a novel gravi-volumetric method with permanganate. A series of fractions was obtained by fusion of praseodymium nitrate with nitre, but all gave the same number, Pr = 140·95, so that no decomposition into different earths took place. (3) By synthesis of the sulphate. A known quantity of the oxalate containing a known quantity of the oxide, Pr_2O_3, as determined in (1) and (2) was converted into the sulphate by the usual method. Different fractions did not show any sign of decomposition, but the atomic weight deduced in this way was lower than in (1) and (2), being only Pr = 140·78. As in the case of lanthanum it was found that praseodymium sulphate also does not part completely with the slight excess of free sulphuric acid (acid sulphate of Wyrouboff) on heating and therefore shows an acid reaction. Using a normal sulphate tinted with ethyl orange as indicator as the standard of comparison, this excess of sulphuric acid was determined with *N*/20 sodium hydroxide. The result of series (4) in which the error due to the hygroscopic nature of the oxide and of the anhydrous sulphate was eliminated gave the atomic weight Pr = 140·93. Excluding series (2) as it was vitiated by an error which became known only at a later period, and which caused Jones and v. Scheele to obtain the incorrect number Pr = 140·4—140·5, the mean result is Pr = 140·94.

The above results only prove that the equivalent of praseodymium is 47, so that the atomic weight is either $Pr^{I} = 47$ or $Pr^{II} = 94$, $Pr^{III} = 141$, $Pr^{IV} = 188$ or $Pr^{V} = 235$. In order to solve this question the molecular weight of the anhydrous chloride was determined by the ebullioscopic method, absolute alcohol being used as the solvent. Several determinations gave numbers for the molecular weight approaching 247·4 (this corresponds to $PrCl_3$), so that this fact, together with the analogies pointed out three years ago (*Proc.*, 1898, 14, 71), proves definitely that the true atomic weight of praseodymium is Pr = 140·94.

49. "On praseodymium tetroxide and peroxide." By B. Brauner.

When the author published his preliminary note (*Proc.*, 1898, **14**, 71) he left unsolved many of the problems connected with the black higher oxide which he was the first to prove possessed the formula Pr_2O_4. This oxide was subjected to a new and careful investigation. The only method for obtaining this oxide pure is by fusion of the nitrate with nitre, the combustion of the oxalate employed by v. Scheele, giving a very impure compound. The pure praseodymium tetroxide has a sp. gr. of 5·978 (at 20°/4° and in a vacuum); the pure trioxide, Pr_2O_3, has a sp. gr. of 7·068. The molecular volume of $Pr_2O_4 = 57·9$, that of $Pr_2O_3 = 46·7$, hence the volume of the active (the fourth) oxygen atom is +11·2, an unusually large number for the volume of 1 atom of active oxygen. Hence we can understand the great instability of the salts of the type PrX_4. The oxides, Pr_2O_4 and Pr_2O_3 combine to form a complex oxide of the approximate composition Pr_4O_7, or more correctly $Pr_{10}O_{18}$, of sp. gr. 6·704, showing that slight contraction has taken place. The *pure* praseodymium tetroxide does not give the hydrogen peroxide reaction, and is a purely *ozonic* oxide. It gives free chlorine with hydrochloric acid, ozonised oxygen with oxy-acids; in acid solution, it oxidises cerous salts to ceric salts, manganous salts to permanganic acid, and gives the characteristic violet coloration with a solution of strychnine in sulphuric acid. It "catalyses" with hydrogen peroxide in acid solution.

Praseodymium nitrate yields with hydrogen peroxide, with sodium peroxide and an alkali, the hydrated real peroxide, Pr_2O_5, belonging to the *antozonic* oxides. To the same type belongs the acetate the composition of which may be represented by the formula $Ac_2{:}Pr^{III}{\cdot}O{\cdot}O{\cdot}O{\cdot}Pr^{III}{:}(OH)Ac + H_2O$.

The maximum valency of praseodymium is tetrad, like that of cerium. The corresponding oxides have a smaller volume (greater density) than those of cerium, which it resembles most of all elements, but no place has been found in the periodic system for an element possessing the physical and chemical properties of praseodymium and its compounds.

50. "Note on neodymium." By B. Brauner.

Applying the "sulphate method" for the determination of the atomic weight of neodymium as in the case of lanthanum and praseodymium, the neodymium material, purified with sodium sulphate, gave the atomic weight Nd = 143·80, the correction due to the presence of the acid sulphate being determined experimentally. Neodymium forms (in the dry way) a higher oxide, Nd_2O_4, with such an extremely feeble

tension (potential) of the active (fourth) oxygen atom that on liberation with acids this oxygen passes through ferrous salt solutions without oxidising them. Many other rare earths will probably form higher oxides of the same type, but their preparation and investigation offer great difficulties. These acids seem to represent the extreme limit of *ozonic* oxides.

In addition to this, neodymium yields purely *antozonic* compounds of the type R_2O_5, like the hydrated peroxide and the peculiar acetate, $Ac{:}Nd^{III}{\cdot}O{\cdot}O{\cdot}O{\cdot}Nd^{III}{:}(OH){\cdot}Ac + H_2O$, strictly analogous to the corresponding praseodymium compounds.

The difficulties of finding a place for neodymium in the periodic system are even greater than in the case of praseodymium.

51. "Contribution to the chemistry of thorium." By B. Brauner.

The results obtained on studying the behaviour on hydrolysis of the salt, $Th(C_2O_4{\cdot}NH_4)_4 + 7H_2O$ (*Trans.*, 1898, **73**, 951), were applied to the fractionation and purification of commercial thorium compounds. In this way, at the one end of the series the most basic, positive fractions were obtained, that is, those which are most easily hydrolysed and termed Th_α, and at the other the most acid, negative fractions which are most easily hydrolysed, and which are called Th_β.

After removing the trivalent rare earths by methods indicated (*loc. cit.*), the atomic weight of thorium contained in the most basic (positive) fractions was determined, and the numbers $Th_\alpha = 233{\cdot}5$ (by the oxalate method) and $Th_\alpha = 233{\cdot}3$—$233{\cdot}7$ (by the sulphate method were found.

The most negative (Th_β) fractions gave at first the atomic weight $Th_\beta = 232{\cdot}5$, and this by further purification of the material decreased to $Th_\beta = 232{\cdot}0$ and $231{\cdot}9$. By working up a much larger quantity of material and trying to determine the atomic weight by the oxalate method, abnormal results were obtained owing to the easy formation of basic salts by the Th_β material, a property not possessed by the ordinary thorium salts. An extremely careful set of analyses by the oxalate method gave $R^{IV} = 236{\cdot}3$ whereas an analysis of the sulphate precipitated by alcohol from an aqueous solution which must be strongly hydrolysed gave $R^{IV} = 280{\cdot}7$. Ordinary thorium sulphate owing to only partial hydrolysis of the sulphate in the aqueous solution gives under the same conditions of precipitation $R^{IV} = 234{\cdot}6$, that is, only a slightly basic salt.

On further fractionation of the most negative (Th_β) fraction, a material was obtained which, after conversion into the normal sulphate and its analysis, gave $Th_\beta = 220$. This decrease of the atomic weight from 232 to 220 is accompanied by a decrease in the density of the

oxide from 10·2 to 9·6 along with the property of the β-fractions of easily forming basic salts—a property exhibited by no known earth, with the exception of zirconium, which, however, cannot be present, may be regarded as proving the complex nature of thorium. These thoroughly established facts have been known to the author for years, but he abstains from further conclusions, especially as the study of the very complicated spectral phenomena connected with the above research proceeds but slowly.

52. "Pheno-α-ketoheptamethylene and its derivatives." By F. S. Kipping and A. E. Hunter.

The authors have continued the investigation of the ketone obtained by the action of aluminium chloride on phenylvaleric chloride (Kip- and Hall, *Proc.*, 1899, **15**, 173), and have proved that it contains a seven carbon atom ring condensed with benzene in the ortho-position, as on oxidation with dilute nitric acid it yields *o*-phthalic acid.

Pheno-α-ketoheptamethylene oxime crystallises from dilute alcohol in lustrous needles melting at 108—109°; the corresponding phenylhydrazone and *p*-bromophenylhydrazone do not crystallise readily, and are oxidised on exposure to the air.

Pheno-α-aminoheptamethylene, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CH(NH_2)\cdot CH_2\end{matrix}$, is obtained when the oxime is reduced with sodium amalgam in acetic acid solution; it is a strongly basic, colourless liquid which absorbs carbon dioxide on exposure to the air.

The *hydrochloride*, $C_{11}H_{15}N,HCl$, is only moderately soluble in cold water, and crystallises in small prisms which do not melt at temperatures below 250°.

The *platinichloride*, $(C_{11}H_{15}N)_2,H_2PtCl_6$, forms orange needles. The *picrate* crystallises well and is only sparingly soluble. The *sulphat-* forms thin, transparent plates and melts at about 229°; like the *oxalate*, it is only moderately soluble in water.

The *benzoyl* derivative crystallises in felted masses of needles melting at 171—172°.

53. "Note on diphenyldinitroethylene." By J. J. Sudborough.

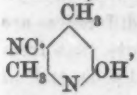
In the last number of the *Berichte* (1901, **34**, 619), Julius Schmidt describes two stereoisomeric *s*-diphenyldinitroethylenes, $NO_2\cdot CPh{:}CPh\cdot NO_2$, the one melting at 186—187° and the other at 105—107°. Both compounds were obtained by the direct addition of nitrogen peroxide to tolane. The compound melting at 105—107° was prepared by the author several years ago (*Diss.*, 1893; *Trans.*, 1897, **71**,

223; Richter's *Lexicon II*, 1422) by the addition of nitrogen peroxide to monochlorostilbene and the subsequent elimination of hydrogen chloride. The melting point was given as 104—105° and it crystallised in sulphur-yellow prisms and pyramids resembling those described by Schmidt. The molecular weight was determined and the action of bromine investigated but no dibromide was isolated, and no definite reduction products were obtained, but according to Schmidt the chief reduction product is $a\beta\gamma\delta$-tetraphenyl piperazine.

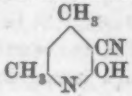
54. "Para- and ortho-cyanohydroxy-derivatives of pyridine." By J. Moir, M.A., B.Sc.

Holtzwart, by boiling an aqueous solution of the polymeride of acetonitrile, $C_4H_6N_2$, obtained a condensation product, $C_8H_8ON_2$, which he described merely as melting above 230°.

The author has further investigated this substance which is marked by extraordinary stability, and finds that it melts at 305° (corr.) and that it is, in all probability, a cyanohydroxylutidine of the constitution



, isomeric with the compound



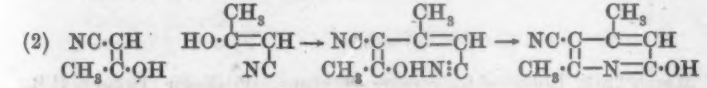
(m. p. 288—289°) which Guareschi obtained from acetylacetonamine with cyanoacetic ester.

This constitution is based on the fact, among others, that when hydrolysed by heating with strong solution of hydrogen bromide at 170°, it yields pseudolutidostyril, by exchange of hydrogen for cyanogen. All attempts to produce the intermediate carboxy-acid have failed. This acid has been obtained by Collie by an analogous reaction. Attempts to synthesise the cyano-compound from Collie's acid and ester have also been without result, owing to the stability of the compounds in question.

The mechanism of the condensation is evidently as follows:

(1) $CH_3 \cdot C(NH_2) : CH \cdot CN + H_2O \rightarrow CH_3 \cdot C(OH) : CH \cdot CN$ (cyanoacetone).

(2)



The author has also found that the supposed third isomeride of $C_8H_8ON_2$, prepared by von Meyer from a compound, $C_8H_9N_3$, by the action of nitrous acid, is in reality identical with Holtzwart's isomeride. It follows that $C_8H_9N_3$ is 3-cyano-2 : 4-dimethyl-6-aminopyridine.

A careful physical and chemical comparison of Holtzwart's and

Guareschi's isomerides has been made, and although they resemble one another very closely, they were found to be different.

Both compounds form white, sparingly soluble needles of a very bitter taste; they are not basic, but form soluble derivatives with the alkali-metals, and cannot be directly methylated. Both resist hydrolysis with strong alkalis and acids, but give pseudolutidostyril with hydrogen bromide. They differ in their action on polarised light, and when mixed the melting point is depressed. Different compounds are obtained from each by bromination and nitration. The bromo-derivative of Holtzwart's isomeride melts at 307—308°; that of Guareschi's compound at 260—262°. The nitro-compound of Holtzwart's isomeride melts at 262° and forms yellow salts; that of Guareschi's compound melts at 271°, and forms white salts which give yellow solutions. This agrees well with the formulæ assigned to them, the former having the nitro-group in the ortho-position relatively to the hydroxyl, while in the latter case it is in the para-position.

Again, Guareschi's isomeride can be hydrolysed by warm fuming sulphuric acid, or by fusion with potash, whereas Holtzwart's isomeride cannot.

On reducing the two nitro-compounds, characteristic differences are obtained in the reactions of the amino-derivatives; while that from Guareschi's isomeride gives no colour with ferric chloride, and in alkaline solution has a strong blue fluorescence, the amino-derivative of Holtzwart's isomeride gives an indigo colour with ferric chloride, and becomes cherry-red in presence of ammonia. These reactions are also given by Collie's acid after nitration and reduction, whence it follows that they have the same configuration.

The author failed to obtain, by the action of phosphorus pentachloride on his compound, the substance $C_8H_6N_2$, described by Holtzwart.

From the pseudolutidostyril obtained in these experiments, the following derivatives were obtained:

(1) 3 : 5-*Dibromo-ψ-lutidostyril*, melting at 253° (corr.).
(2) 5-*Nitro-ψ-lutidostyril*, melting at 254° (corr.).
(3) 3-*Nitro-ψ lutidostyril*, melting at 196° (corr.).

March 28th, 1901. Anniversary Meeting. Professor THORPE, C.B., F.R.S., President, in the Chair.

Dr. JOWETT and Mr. WERNER were appointed Scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's address.

The PRESIDENT, in beginning his address, said that the Chemical Society was founded about four years after the accession to the throne of the Gracious Lady whose recent loss they deplored, and the memory of whose virtues and worth as a woman and as a monarch would for ever abide with them. He was proud to think that this Society, in so far as it had ministered to the progress of chemistry, may have contributed in some measure to the lustre of a reign so pre-eminently associated with the development and spread of science in this country, and with the extension of those arts which rest upon chemistry. The Society was not unmindful of what the science owed to the Royal Family, and in particular to the late Prince Consort, whose appreciative interest in the fortunes of the Royal College of Chemistry, of which he was the President, and whose friendship for the eminent man who made it the first organised school of chemical research in this country, had directly ministered to its own activity, welfare, and usefulness. The Society had sought to give utterance to these sentiments in an Address, which it ventured to submit to his Majesty on his accession to the Throne, and in respectfully tendering its congratulations, and in offering its homage, it expressed the hope that his reign would be marked by discoveries in the science it represented not less brilliant than those which characterised the reign of his illustrious mother.

The numerical strength of the Society was as follows:

Number of Fellows, March 29th, 1899		2292
" " since elected		117
" " reinstated by Council		5
		2414
Removed on account of non-payment of two annual subscriptions	28	
Withdrawn	31	
Deaths	20	79
Number of Fellows, March 28th, 1901		2335
Foreign Members		33

The names of those removed were:—Carl Bennert; G. F. Brindley; R. E. Brown; James Crowther; W. B. Edwards; Sidney Fawns; L. F. Goldstand; D. A. Griffiths; W. T. Gronow; R. Glode Guyer; W. G. Lasseter; H. E. Law; Herbert Lloyd; J. A. MacFarlane; E. MacSwiney; S. M. Martin; W. B. McVey; E. E. Milnes; H. J. Monson; R. H. Owen; J. B. Reid; H. J. Phillips; James Speakman;

Thomas Stormouth; J. B. Thornley; H. W. Wallis; A. W. Warwick; R. H. Wilson.

The following have withdrawn:—E. L. Allhusen; J. Allport; Frank Bastow; F. Barker Cooke; G. H. Cross; Sir Michael Foster; J. Frost; H. E. Gardner; J. F. H. Gilbard; William Goddard; Frederic Gothard; Robert Hamilton; Harold Ellershaw Head; William M. Heller; Henry Leonard Hinnell; Alfred Kingsby Howard; Edgar Joseph; A. E. Lewis; C. T. Macadam; Fred Marsden; James Mason; John Charles Platts; Percy Morrice Randall; S. G. Rosenblum; Edward Rosling; James Spencer; James H. Stebbins; Sydney Steel; William Ward; A. Swainson Waterfield; P. A. Wier.

The following have died:—Edmund Atkinson; John Borland; Alfred Hunter Boylan; William Harcourt Branscombe; Sir John Conroy; Henry Howard Crawley; Thomas Flower Ellis; Frank W. Harris; Herbert A. Hotblack; Sir John Bennet Lawes; Stevenson Macadam; Frederick Alfred Manning; William McConnell; William Parsons; Richard Reynolds; Saville Shaw; George Smith; C. J. H. Warden; Augustus A. Wood; Thomas M. Wyatt.

The President offered on behalf of the Society its warm congratulations to its former President and Treasurer, Dr. Russell, on the attainment this year of his jubilee as a Fellow of the Society. Mr. Nevil Story Maskelyne, a former Vice-President of the Society, Sir David Gamble, C.B., and Mr. Edward Riley were also congratulated on reaching this anniversary.

During the year, the Society had joined in the commemoration of the 40th year of the doctorate of Professor Markownikoff of Moscow, one of its distinguished Foreign Members.

Since the last Anniversary, 182 communications had been made to the Society, a number greater than in any preceding year. In character, variety, and importance they compared not unfavourably with the contributions of any former period. Abstracts of all these had appeared in the *Proceedings*, while 106 have already been published in the *Transactions*. The volume of *Transactions* for 1900 contained 127 memoirs, occupying 1334 pages; in the preceding year 120 papers were published, occupying 1166 pages. The President drew particular attention to the desirability of brevity in the papers communicated to the Society.

The volumes for 1900 contain 3758 abstracts of papers, published mainly in Continental journals, occupying 1492 pages, arranged as follows:—

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	712	1355

PART II.

General and Physical Chemistry		467
Inorganic Chemistry		383
Mineralogical Chemistry		174
Physiological Chemistry		336
Chemistry of Vegetable Physiology and Agriculture		368
Analytical Chemistry		675
	780	2403
Total in Parts I. and II.	1492	3758

The number of abstracts dealt with in 1899 is 141 more than in the preceding year, though occupying 304 pages less.

The volume for 1900 contained no less than four Memorial Lectures, giving an account of the life-work of Victor Meyer, Bunsen, Friedel, and Nilson. The Council had determined to issue those Memorial Lectures which had appeared up to the end of 1900 in a separate form. The President in this connection paid a special tribute to the late Prof. FitzGerald, who had delivered the Helmholtz Memorial Lecture, one of the most weighty of the series.

A special reference was made to the bearing of the Copyright Bill upon the Society as a publishing agency.

As regards the Library, 810 books had been borrowed, as against 790 last year; and 95 books, 327 volumes of periodicals, and 30 pamphlets had been added, as against 114 books, 397 volumes of periodicals, and 27 pamphlets in the preceding year.

A number of books and periodicals not bearing in any way on the work of the Society had been removed from the library. Some proportion of these had been offered to and accepted by the British Museum; the remainder will be disposed of either by presentation to kindred societies or otherwise. The need of shelf room was pressing in view of the fact that the present accommodation would be exhausted in two years. The library catalogue was within sight of completion. It included 6,300 author entries and nearly as many subject entries. An estimate for printing was in preparation.

The President, referring to the result of the voting on the question of the day and hour of meeting, said the Committee had reported to the Council that the returns, however analysed, showed such a large

majority in favour of the proposed change, that the Council had decided that it should be provisionally tried during the coming session. The Ordinary Meetings of next session would therefore be held on the first and third Wednesdays of the month, at 5.30 p.m.

A reference was made to the movement for a uniform system of atomic weights, and it was announced that the Atomic Weights Committee had decided to recommend (1) that O = 16 be taken as the basis of calculation of atomic weights; (2) that in assigning a number as the atomic weight of any element only so many figures should be employed that the last may be regarded as accurately known to one unit in that figure.

Grants amounting to £160 had been made from the Research Fund in aid of chemical investigation.

Dr. ARMSTRONG proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the *Transactions*.

Prof. SMITHELLS seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Prof. TILDEN, F.R.S., the Treasurer, in giving an account of the Balance Sheet which he laid before the Society, duly audited, said :—

The receipts had been :—By admission fees and subscriptions, £4290; by sale of Journal and advertisements, £880 12*s.* 9*d.*; and by dividends on invested capital, £464 14*s.* 4*d.* The total receipts from all sources amounted to £5668 19*s.* 8*d.* The expenses had been :—On account of the Journal, £3512 9*s.* 11*d.*; on account of the Proceedings, £250 15*s.*; on account of the preparation of a new Catalogue, £51 16*s.* 4*d.*; on account of the Library, £238 15*s.* 11*d.*; House expenses, £210 9*s.* 11*d.*; the total expenditure being £4832 3*s.* 9*d.*

The TREASURER, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. PAGE.

Prof. EMERSON REYNOLDS, F.R.S., proposed a vote of thanks to the Officers and Council.

Prof. COLLIE, F.R.S., seconded the motion, which was unanimously adopted. Prof. DUNSTAN, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected :—

President: J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, Bart., G.C.V.O., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.;

James Dewar, M.A., LL.D., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe, D.C.L., LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., Ph.D., D.Sc., LL.D., For.Sec.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: E. Divers, M.D., D.Sc., F.R.S.; C. E. Groves, F.R.S.; Prof. Herbert McLeod, F.R.S.; Prof. H. A. Miers, M.A., F.R.S.; T. Purdie, Ph.D., F.R.S.; T. Stevenson, M.D.

Secretaries: Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: William A. Tilden, D.Sc., F.R.S.

Other Members of Council: H. Brereton Baker, M.A.; F. D. Chattaway, Ph.D., D.Sc.; Frank Clowes, D.Sc.; A. W. Crossley, Ph.D., D.Sc.; A. E. Dixon, M.D.; Prof. J. J. Dobbie, M.A., D.Sc.; H. J. H. Fenton, M.A., F.R.S.; M. O. Forster, Ph.D., D.Sc.; D. Howard; S. U. Pickering, M.A., F.R.S.; W. J. Pope; James Walker, D.Sc.

ANNIVERSARY DINNER.

The Anniversary Dinner of the Society took place at the Whitehall Rooms, on Wednesday, March 27th, at 7 p.m., when the following Fellows and their guests dined together:—

Abney, Sir W. de W., K.C.B., F.R.S.
Adams, Mr. M. A.
Alldred, Mr. C. H.
Atkinson, Mr. G. D.

Barlet, Mr. S.
Beadle, Mr. Clayton.
Beaven, Mr. E. S.
Bevan, Mr. E. J.
Blakesley, Mr. G. H., *Master of the Mercers' Company.*
Bowley, Mr. J. J.
Brough, Mr. B. H.
Brown, Dr. H. T., F.R.S.

Callendar, Prof., F.R.S., *Treasurer of the Physical Society.*
Carr, Mr. F. H.
Carteighe, Mr.
Central News.
Chancellor, The Rt. Hon. the Lord.
Chapman, Mr. A. C.
Church, Sir W. S., Bart., M.D., *President of the Royal College of Physicians.*
Clerk, Mr. D.
Collart, Mr. H.
Collis, Mr. W.
Connah, Mr. J.
Crossley, Dr.

Daily News, The.
Dewar, Prof., F.R.S.
Divers, Prof., F.R.S.
Dixon, Prof. H. B., F.R.S.

Dobbie, Prof.
Donnelly, Sir John, K.C.B.
Dunstan, Prof., F.R.S., *Hon. Secretary.*
Dyer, Dr.
Dyer, Sir W. T. Thiselton-, K.C.M.G.

Epps, Mr. James.

Farmer, Prof., F.R.S.
Fenton, Mr. H. J. H., F.R.S.
Forster, Dr.
Fowler, Rev. Prof., *Vice-Chancellor, University of Oxford.*
Furneaux, Mr. J. R., *Master of the Leathersellers' Company.*

Greenaway, Mr. A. J., *Sub-Editor.*
Griffith, Mr. G.
Groves, Mr. C. E., F.R.S.
Guttmann, Mr. O.

Hall, Mr. Samuel.
Harrison, Mr. E. F.
Hartley, Mr. H. B.
Harvey, Mr. E. W.
Hehner, Mr. O.
Henley, Mr. F. R.
Hill, Mr. A. Croft.
Hill, Mr. C. A.
Hopkins, Dr. F. Gowland.
Houlding, Mr. W.
Howie, Mr. W. L.
Hutchinson, Mr. C. C.

Jackson, Mr. Henry.
Jones, Mr. H. O.

Kellner, Dr.
Kelvin, Rt. Hon. Lord, G.C.V.O., *President of the Royal Society of Edinburgh, Master of the Clothworkers' Company.*
Kemp, Mr. W. J.
Kempe, Mr. A. B., F.R.S., *Treasurer of the Royal Society.*
Kenny, Dr.
Kohn, Dr.

Le Sueur, Mr. H. R.
Lewkowitsch, Dr.
Ling, Mr. A. R.
Lockyer, Sir Norman, K.C.B.
Luxmoore, Dr.

MacEwan, Mr. P.
McLeod, Prof., F.R.S.
MacMahon, Major, R.A., F.R.S.
Markham, Mr. E.
Martindale, Mr. W.
Maxwell, Rt. Hon. Sir Herbert, Bart., M.P.
Meldola, Prof., F.R.S., *Foreign Secretary.*
Messel, Dr.
Mond, Dr. R.
Moody, Dr.
Morley, Dr. Forster.
Morris, Dr. G. H.
Morton, Mr. E. H.
Mowatt, Sir Francis, G.C.B. *Secretary to the Treasury.*
Müller, Dr. Hugo, F.R.S.

Nicholson, Dr.

Orton, Dr.

Page, Mr. F. J. M.
Perkin, Dr. W. H., F.R.S.
Pope, Mr. W. J.
Power, Dr.
Prideaux, Sir Walter, *Clerk of the Goldsmiths' Company.*
Pritchard, Prof.

Ramsay, Prof., F.R.S.
Reynolds, Prof. J. Emerson, F.R.S., *President-Elect.*
Robbins, Mr. J.
Roberts, Sir Owen, *Clerk of the Clothworkers' Company.*
Robertson, Dr.
Roscoe, Sir Henry, F.R.S., *Vice-Chancellor, University of London.*
Roundell, Mr. C. F.
Russell, Dr. W. J., F.R.S.
Ryder, Mr. G. L., C.B., *Chairman H.M. Board of Customs.*

Sadler, Col., M.P.
Salamon, Mr. A. Gordon.
Schweich, Mr. E.
Scott, Dr., F.R.S., *Hon. Secretary.*
Scott, Mr. E. L., *Clerk of the Salters' Company.*
Seaton, Dr. E. C.
Smithells, Prof.
Spiller, Mr.
Spooner, Mr. F.
Standard, The.
Steele, Mr. R., *Assistant-Secretary and Librarian.*
Stevenson, Dr. T.
Strutt, The Hon. R. J.
Sullivan, Dr. Washington.
Swan, Mr. J. W., F.R.S., *President of the Society of Chemical Industry.*

Thompson, Prof. S. P., F.R.S., *President of the Physical Society.*
Thomson, Prof., F.R.S., *President of the Institute of Chemistry.*
Thorpe, Prof., C.B., F.R.S., *The President.*
Tilden, Prof. F.R.S., *Treasurer.*
Times, The.
Tutton, Mr. A. E., F.R.S.

Voelcker, Dr. J. A., *President of the Society of Public Analysts.*
Wade, Mr. J.
Watson, Mr. C.
Werner, Mr. E. A.
Wilkinson, Mr.
Williams, Mr. G., R.N.
Wyllie, Mr. C. W.
Wynne, Dr., F.R.S., *Editor.*

The following toasts were proposed :—

By the PRESIDENT.

1. His Most Gracious Majesty the King.
2. Her Majesty the Queen Alexandra, their Royal Highnesses the Duke and Duchess of Cornwall and York, and the other Members of the Royal Family.

By the TREASURER.

3. The Houses of Legislature, coupled with the names of the Rt. Hon. The LORD CHANCELLOR, and the Rt. Hon. Sir HERBERT MAXWELL, Bart., M.P., F.R.S.

By the Rt. Hon. LORD KELVIN, G.C.V.O., F.R.S., *President of the Royal Society of Edinburgh, and Master of the Clothworkers' Company.*

4. Prosperity to the Chemical Society.

By Professor DEWAR, F.R.S.

5. The Learned and Scientific Societies, coupled with the names of Mr. A. B. KEMPE, *Treasurer of the Royal Society*, and Professor SILVANUS P. THOMPSON, F.R.S., *President of the Physical Society.*

By Professor EMERSON REYNOLDS, M.D., F.R.S., *President-Elect of the Chemical Society.*

6. The Guests, coupled with the names of Sir W. S. CHURCH, Bart., M.D., *President of the Royal College of Physicians*, and Sir FRANCIS MOWATT, G.C.B.

By Sir HENRY E. ROSCOE, F.R.S., *Vice-Chancellor of the University of London.*

7. The retiring President.

In proposing the loyal toasts, THE PRESIDENT, while paying the Society's tribute to the late Queen, said they could have no manner of doubt that the King would worthily follow in her footsteps. That the King would long rule over the splendid heritage to which he had succeeded, and that his reign might be marked with the same full measure of prosperity, intellectually and morally, which had graced the reign of Victoria, was their constant hope and confident anticipation.

THE TREASURER, Professor Tilden, in proposing the toast of the Houses of Legislature, said they did not seek the honour of the presence of so many members of both Houses at their dinner that evening solely for the purpose of enjoying their society. The fact was the Chemical Society, old and respectable as it was, had to give a sort of account of itself in the face of the world, and nowhere was it so important that the objects of the Society, and the benefits they thought it conferred upon the community, should be recognised as in the Houses of Legislature. Some of them were rather anxious as to the part which science had to play and the position which science was to occupy in the national programme. Science demanded a much more influential place in the councils of the nation than had hitherto been granted it.

The LORD CHANCELLOR, in responding for the House of Lords, said he had feared from the Treasurer's speech that they were about to be subjected to a quantitative and qualitative analysis, but was glad to see it pass off into a homily upon the importance of infusing into Parliament a more scientific spirit. He was always glad to use the phrase Parliament, because although, for obvious purposes, it was desirable that it should be divided into two Chambers, he always liked to regard that great instrument of human enlightenment and freedom as being one, and he would lament anything which interfered with the working of that great constitutional machine. He believed that the House of Commons had that day been distinguishing itself in its energy to procure chemically pure beer. (Laughter.) He, unfortunately, had no such claim to make for the House for which for the moment he had the honour to respond. He did not believe they had been dealing either with beer or science during this Session, except so far as military science might be supposed to demand public attention. He accepted with the most perfect good faith the exhortation which he had received from the proposer of the toast, and so far as he could influence either public opinion or the action of the House of Lords, he would never forget what they owed to science. He had heard it whispered—he would not say by unkind friends—that their work in manufacturing Acts of Parliament was not absolutely perfect, but the more they advanced in the science of language, in

perfecting precision in organising human thought and reasoning, the plainer they would make to the popular understanding the meaning of an Act of Parliament. Nothing could more induce to the making of clear laws than a scientific education, which would bring about an assiduity of reasoning and clearness of thought.

Sir HERBERT MAXWELL, Bart, M.P., in responding for the House of Commons, said though much had been said in condemnation of that House he submitted that its present Members were not worse than those who had gone before. Though they might conduct their business in a way which would disgrace a self-respecting company, they were not so indifferent to the work of scientists as they appeared to be. They would, for instance, as soon condemn a witch to be burnt as discuss a subject of a scientific nature, such as that which had occupied them that afternoon, without taking the advice of the experts of the question. He asked that they would rather judge of the result of their labours than the way in which that result was attained. He took the opportunity of specially thanking the Chemical Society for the aid and hospitality it had recently afforded the Committee on Food Preservatives, of which he was Chairman.

Lord KELVIN, in proposing the toast of THE CHEMICAL SOCIETY, said he was perfectly appalled at the magnitude of the work he was asked to commend to their notice. When he thought of all that had been done in chemistry during the last century, he was convinced he would in no way be exaggerating when he said that chemistry was the first and last science of the nineteenth century. It only began to exist as a science at the close of the eighteenth century. He was a physicist and he could assure them that physicists had to go to chemistry all through their work. The physicist wanted to measure everything, and now in particular they wanted to know the weight of an atom of hydrogen and the number of molecules in a litre of hydrogen. They were, he was glad to say, in a fair way of learning it, thanks to the labours of chemists. Chemists must stick to dynamics. The chemist had to do with the forces between particles of matter from the hundred-millionth of a gram in weight to the thousand millionth, and had to look to the forces between them, and tell the number of their particles in a litre of water or beer, and say how many of those atoms were arsenic, and how many atoms of arsenic might be allowed. They had learned within the month that some amount of arsenic might be allowed—that without arsenic man could not exist, that an essential in the composition of the human body was the seventeen-hundredth of a gram of arsenic in the thyroid gland. Chemistry was the first and the last science of the nineteenth century, and only recently had given them what ancient chemists would have been glad to have seen—namely, liquid air and liquid hydrogen. He referred

eloquently to the work of the great chemists of the past, especially of the first president of the Society, Professor Graham, and to that of Lord Rayleigh and Professors Ramsay and Dewar. To their labours the physicist owed much, and there was no reason whatever why chemistry and physics should not go hand in hand, helping one another and working cordially together for the advancement of knowledge. Some of the work of the physicist was looked upon as drudgery. Chemists knew a great deal about drudgery too, and did not shrink from it. Lord Rayleigh devoted himself to working painfully and laboriously at an object which looked trivial, the finding of the density of atmospheric nitrogen, and he discovered that it contained a gas that had never even been suspected before. That was a triumph for drudgery. In looking back to the early history of the Chemical Society he took some pride in thinking that Glasgow took its part, in that it provided the first president, and that Dr. Thorpe had been Professor of Chemistry at the Andersonian Institute there. The Chemical Society though but young, only 61 years old, had a glorious past, and he believed a splendid and prosperous future before it.

The PRESIDENT, in reply, said no matter how they regarded the Society, whether from the point of view of its numerical strength or from the character of its scientific output or from the lower ground of its financial condition, he thought there was no constitutional infirmity about it. This happy result was largely to be attributed to that constant accession of strength they gained in the increase of membership. There was no English chemist of note who was not proud of being a member of their body, whilst they had in their ranks almost every foreign chemist of prominence. The honorary membership of their Society was a distinction as highly prized as any mark of recognition which a body of scientific workers could bestow. There were signs of many changes in the chemical world, but whatever the future might have in store for them, he who occupied the presidential chair in the year 2001, and who in ushering in the new century sought to know what was being done when the preceding century was dying, would, he was convinced, do them the justice to recognise that they who collectively made up that body corporate were, according to their several rights and within the measure of their individual powers, doing what within them lay to further the true object of their calling as men of science, the attainment of the truth for the sake of the truth.

Professor DEWAR, in proposing the toast of the learned and scientific societies, said that whenever any body of men had associated themselves for the purpose of discovery, invention, or the verification of truth, then the Chemical Society was most desirous of recognising the advantage of their labours on behalf of the community and of chemistry

especially. Chemists were particularly desirous of recognising the great benefits which accrued from the corporate action of so many minds in the multitudinous departments of scientific work. He spoke of the dangers of exaggerating the importance of personality in matters of scientific research, as scientific work was always based on the labours of the past.

Mr. A. B. KEMPE, Treasurer of the Royal Society, in reply, said there was one point on which the progress of their Society was not so satisfactory as he could wish it to be. That was in the matter of financial support. It was true they had much to thank private beneficence for, and he thought it was a matter of congratulation that His Majesty's Government had in the person of Mr. Balfour recognised the value of pure science. As Treasurer of a scientific society, however, he felt, and he was sure treasurers of other societies felt the same, that they might promote the interests of mankind rather more than they did at present, if they had a little more money to devote to the work.

Professor S. P. THOMPSON, F.R.S., referred particularly to the great work chemists had done in the matter of artificial illumination. He trusted the century now opening would see still greater advances and that the scientific bodies wherever their work seemed to cross or coincide would work hand in hand for the good of all.

Professor EMERSON REYNOLDS, President-Elect, proposed the toast of the Guests, which was responded to by Sir W. S. CHURCH and Sir FRANCIS MOWATT.

Sir HENRY ROSCOE proposed the health of the Chairman.

ADDITIONS TO THE LIBRARY.

I. Donations.

Coux, H. de la. L'eau dans l'industrie. Paris 1900.
From the Publishers.

Dibdin, W. J. Lime, mortar and cement: their characteristics and analyses, with an account of artificial stone and asphalt. London 1901.
From the Author.

Perkin, F. M. Qualitative chemical analysis, organic and inorganic. Ill. London 1901. From the Author.

Shenstone, W. A. The elements of inorganic chemistry, for use in schools and colleges. Ill. London 1901.

—— Laboratory companion for use with Shenstone's inorganic chemistry. London 1901. From the Author.

II. By Purchase.

Fränkel, Sigmund. Die Arzneimittel-Synthese auf Grundlage der Beziehungen zwischen chemischum Aufbau und Wirkung. Berlin 1901.

Jüptner, H. F. v. Grundzüge der Siderologie. 1st part. Die Konstitution der Eisenlegierungen und Schlacken. Ill. Leipzig 1900.

Meyer, Arthur. Die Grundlagen und die Methoden für die mikroskopische Untersuchung von Pflanzenpulvern. Ill. Jena 1901.

Bois-Reymond, E. du. Vorlesungen über die Physik des organischen Stoffwechsels. Ill. Berlin 1900.

Wischin, R. A. Die Naphthene (cyklische Polymethylene des Erdöls) und ihre Stellung zu anderen hydrürten cyklischen Kohlenwasserstoffen. Braunschweig 1901.

Ashmole, Elias. Theatrum Chemicum Britannicum. London 1652.

Ripley reviv'd : or, an exposition upon Sir George Ripley's hermetico-poetical works. Written by Eirenæus Philalethes. London 1678.

At the next meeting, on Thursday, April 18th, 1901, the following papers will be communicated :—

"Researches on moorland waters. Part II. On the origin of the combined chlorine." By W. Ackroyd.

"Robinin, violaquercitrin, and osyritrin." By A. G. Perkin.

"Preparation of orthodimethoxybenzoin, and a new method of preparing salicylaldehydemethylether." By J. C. Irvine.

"Action of alkyl haloids on aldoximes and ketoximes. Part II." By Wyndham R. Dunstan and E. Goulding.

"The supposed existence of two isomeric triethyloxamines." By Wyndham R. Dunstan and E. Goulding.

"Nitrocamphene, aminocamphene, and hydroxycamphene." By M. O. Forster.

"Action of hydroxylamine on the anhydrides of bromonitrocamphane." By M. O. Forster.

"The influence of cane sugar on the conductivities of potassium chloride and potassium hydroxide, with evidence of salt formation in the latter case." By C. J. Martin and O. Masson.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 236.

April 18th, 1901. Professor EMERSON REYNOLDS, F.R.S., President, in the Chair.

Messrs. B. F. Howard, L. Dobbin, W. H. Oates, and Maj.-Gen. Waterhouse were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Guy Ashwell, Standard Bank, Bulawayo; Thomas Aspinall, 42, Gilnow Road, Bolton; William George Aston, 4, Dalkeith Road, Ilford; Edwin Sloper Beaver, 5, Bonham Terrace, Warminster; Fred Bedford, 9, Market Place, Sleaford, Lincs.; Arthur Crabtree, 9, Bigg Market, Newcastle-on-Tyne; Daniel McLaren, Brookdale, Grey Street, Stalybridge; John Powell, Balliol House, Wentworth Street, E.; John Davidson Spence, 2, Hawkhill Place, Perth Road, Dundee; William Arthur Whitton, Bristol Brewery, Brighton.

The following certificate was authorised by the Council under bye-law I (3):

Joseph de Verteuil, Clarence Street, Port of Spain, Trinidad, B.W.I.

The following letter has been received from Prof. Markownikoff in reply to the letter of congratulation (p. 1) addressed to him by the Council:

Moscow, $\frac{22nd\ March,}{4th\ April.}$

DEAR SIR,

Some years ago I was highly honoured to be received into the list of Foreign Members of the most appreciated Chemical Society of

London, and am now deeply moved by the new sign of attention and the hearty congratulations of my dear colleagues.

I beg you to convey to them that devotion to our science will not leave me until the very last.

Your respectful obedient servant,

W. MARKOWNIKOFF.

Prof. MELDOLA,
Foreign Secretary.

EXTRAORDINARY GENERAL MEETING.

The PRESIDENT stated that, having received a requisition signed by a sufficient number of Fellows asking that an Extraordinary General Meeting of the Society be called to consider the change of the day and hour of meeting which the Council had decided upon for the ordinary meetings during the ensuing session, he had fixed Wednesday, May 15th, at 8 P.M. for this meeting.

Of the following papers, those marked * were read:

***55. "Action of alkyl haloids on aldoximes and ketoximes. Part II. Alkylated oximes and isoximes and the constitution of aliphatic oximes." By W. R. Dunstan and E. Goulding.**

In a previous paper (*Trans.*, 1897, **71**, 573) the authors showed that the direct action of alkyl haloids on aldoximes and ketoximes results in the formation of alkyl nitrogen derivatives only, these being derivatives of the isoximes $\begin{matrix} RHC{-}NH \\ \diagdown\!\diagup \\ O \end{matrix}$ and $\begin{matrix} R_2C{-}NH \\ \diagdown\!\diagup \\ O \end{matrix}$. When the alkyl haloid acts on the sodium derivatives of the oximes, that is, on the oximes in presence of sodium methoxide, these derivatives of the isoximes are formed, but together with the true ethers of the oximes, RHC:NOH and R_2C:NOH.

The alkyl isoximes are highly unstable, and have been studied chiefly as the compounds they form with sodium iodide. On hydrolysis they furnish the corresponding aldehyde or ketone, together with a β-substituted hydroxylamine. On reduction in the ordinary manner they are converted into the primary amine of the substituted alkyl and the corresponding aldehyde or ketone. By careful reduction with sodium amalgam and acetic acid in alcoholic solution they are changed, by substitution of hydrogen for oxygen, into the corresponding secondary amines. This is a satisfactory method of preparing pure secondary amines.

The alkyl ethers of the oximes are stable liquids. On hydrolysis

they furnish the aldehyde or ketone and an α-substituted hydroxylamine.

Isomeric alkyl derivatives of acetaldoxime, acetoxime, and acetophenoxime were described, and also their hydrolytic and reduction products.

The authors consider that their results support the view that the isoximido-form represents the ordinary structure of the aliphatic oximes, only alkyl nitrogen derivatives being obtained from them by the direct action of alkyl haloids, the hydroxylic structure in the formation of ethers being determined by the formation of the so-called "salts" with highly electro-positive metals. These salts are, however, readily dissociated, so that by acting on them, in alcoholic solution, with the alkyl haloid some alkyl isoxime is always formed from the free oxime present.

***56. "The supposed existence of two isomeric triethyloxamines." By W. R. Dunstan and E. Goulding.**

The triethyloxamine, $(C_2H_5)_3NO$), obtained by the authors (*Trans.*, 1899, **75**, 792, and *Trans.*, 1900, **77**, 1006) was shown to possess properties which differ from those of the compound described by Bewad, to which he assigned the same constitution. This difference has been since investigated and confirmed by Lachman (*Ber.*, 1900, **33**, 1022), who, however, was unable to offer any explanation of it. The question is now settled by the observation that the compound described by Bewad is in reality β-ethyl-*sec*-butylhydroxylamine, as Bewad himself has shown (*Journ. Russ. Phys. Chem.*, 1900, **32**, 455). The triethyloxamine obtained by the authors is at present, therefore, the only known compound having this constitution.

***57. "Nitrocamphene, aminocamphene, and hydroxycamphene." By M. O. Forster.**

1-*Nitrocamphene*, $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot NO_2\end{matrix}$, prepared by heating an alcoholic solution of 1 : 1-bromonitrocamphane with silver nitrate, crystallises from alcohol in long, hard, striated prisms and melts at 56°; it has $[\alpha]_D = +112{\cdot}0°$ in alcohol, and $+137{\cdot}5°$ in benzene. 2 : 1-*Bromonitrocamphane*, $C_8H_{14}<\begin{matrix}CHBr\\ |\\ CH\cdot NO_2\end{matrix}$, obtained when nitrocamphene is treated with hydrobromic acid, crystallises from alcohol and melts at 178°. 1 : 2-*Dibromo*-1-*nitrocamphane*, $C_8H_{14}<\begin{matrix}CHBr\\ |\\ CBr\cdot NO_2\end{matrix}$, produced by the action of bromine on nitrocamphene, crystallises in long, flat,

transparent needles and melts at 195°. 2:1-*Iodonitrocamphane*, $C_8H_{14}<\begin{matrix}CHI\\|\\CH\cdot NO_2\end{matrix}$, prepared from nitrocamphene and hydriodic acid, crystallises in thin, lustrous plates and melts at 118°.

1-*Aminocamphene*, $C_8H_{14}<\begin{matrix}CH\\||\\C\cdot NH_2\end{matrix}$, formed on reducing nitrocamphene with zinc dust and glacial acetic acid, melts at 46°, and boils at 191—192° under 758 mm. pressure; it has $[\alpha]_D = +59{\cdot}7°$ in alcohol. The *sulphate*, *picrate*, *platinichloride*, and the *benzoyl*, *benzylidene*, and *phenylcarbamide* derivatives are well-defined.

1-*Hydroxycamphene*, $C_8H_{14}<\begin{matrix}CH\\||\\C\cdot OH\end{matrix}$, obtained on heating aminocamphene sulphate with potassium nitrite, crystallises in long needles, melts at 74° and boils at 212° under 750 mm. pressure; it has $[\alpha]_D = +34{\cdot}1°$ in absolute alcohol. Hydroxycamphene is indifferent towards alkalis, but warm dilute mineral acids transform it immediately into ordinary camphor.

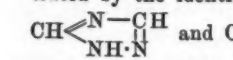
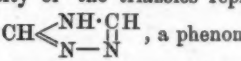
*58. "A contribution to the chemistry of the triazoles." By G. Young and W. H. Oates.

The authors discuss the possibility of isomerism in the triazole series as compared with the pyrazoles.

The following compounds have been obtained:

Benzal-2-methylsemicarbazone, $C_6H_5\cdot CH{:}N\cdot N(CH_3)\cdot CO\cdot NH_2$, m. p. 159—160°; *3-phenyl-1-methylhydroxytriazole*, $C_6H_5\cdot C<\begin{matrix}N\cdot NCH_3\\|\\N{:}COH\end{matrix}$, m. p. 218—219°; *acetyl* derivative, m. p. 72·5—73°, *silver* derivative, $C_9H_8ON_3Ag$; *3-phenyltriazole*, m. p. 118·5—119°; *cinnamal-2-methylsemicarbazone*, m. p. 155°; *styrenylmethylhydroxytriazole*, m. p. 204—205°; *silver* derivative, $C_{11}H_{10}ON_3Ag$; *acetyl* derivative, m. p. 88—89°; *m-nitrobenzalmethylsemicarbazone*, m. p. 207—208°; *m-nitrophenylmethylhydroxytriazole*, m. p. 285—285·5°; *silver* derivative, $C_9H_7O_3N_4Ag$; *benzoyl-4-methylthiosemicarbazide*, $C_6H_5\cdot CO\cdot NH\cdot N{:}C(SH)\cdot NHCH_3$, m. p. 198°; *2-phenyl-1-methyltriazole*, $C_6H_5\cdot C<\begin{matrix}N\cdot N{:}CH\\|\\\text{———}NCH_3\end{matrix}$, m. p. 112—113°; *2-phenyl-1-methylmercaptotriazole*, m. p. 163—164°. Methylsemicarbazide, formed by the action of potassium cyanate on methylhydrazine sulphate, has the methyl group in position (2), $NH_2\cdot N(CH_3)\cdot CO\cdot NH_2$, and not in position (1), $CH_3NH\cdot NH\cdot CO\cdot NH_2$ (compare Brüning, *Ann.*, 1889, 253, 11).

Discussion.

Dr. Silberrad pointed out that Knorr's theory affords a better explanation than that given by the author of facts such as that illustrated by the identity of the triazoles represented by the formulæ  and  , a phenomenon to which attention was drawn on the conversion of dihydrotetrazine into the triazole represented above (Hantsch and Silberrad, *Ber.*, 1900, **33**, 89).

In reply, Dr. Young said that the identity of Freund's triazole with that prepared from tetrazine was in agreement with the view put forward in the paper as to the "amidine" nature of the triazole ring.

59. "Researches on moorland waters. Part II. On the origin of the combined chlorine." By W. Ackroyd.

The object of the investigation has been to discover the origin of the common salt in the water of the Widdop reservoir in Yorkshire, about midway between the two seas, this water being continually removed and as continually replenished from a saltless area of Millstone Grit and Yoredale rocks. The chlorine in the winter rainfall more than accounts for it, and the conclusions arrived at are (1) that the combined chlorine in the reservoir water is wholly derived from rain water; (2) that the quantity of chlorine in the reservoir, whose capacity is 640½ million gallons, closely approximates to a yearly average of 1·188 parts per 100,000, and (3) that in winter the chlorine in the rainfall is in excess of the average for other seasons of the year.

60. "Robinin, violaquercitrin, and osyritrin." By A. G. Perkin.

Robinin, isolated from the flowers of *Robinia pseudacacia* by Zwenger and Dronke (*Ann. Sup. I*, 1861, 257) was considered by them as a glucoside of quercetin. The formula $C_{33}H_{38}O_{20},8H_2O$ is now assigned to the air-dried substance, and its decomposition with dilute mineral acids may be thus represented, $C_{33}H_{38}O_{20} + 4H_2O = C_{15}H_{10}O_6 + 3C_6H_{12}O_6$. The *colouring matter*, $C_{15}H_{10}O_6$, melts at 271—272°, yields a *sulphate*, $C_{15}H_{10}O_6,H_2SO_4$, and a *tetracetyl* derivative, $C_{15}H_6O_6(C_2H_3O)_4$. On decomposition with alkali, phloroglucinol and *p*-hydroxybenzoic acid are formed. It is identical with *kampherol*, which is present as its monomethyl ether, kampheride, in galanga root (*Alpinia officinarum*) (Gordin, *Dissert.*, Berne), and

as glucoside in *Delphinium consolida* (*Proc.*, 1900, **16**, 182). The sugar gave a mixed osazone, from which dextrosazone (m. p. 204—205°) and a more soluble compound, m. p. 190—196° (possibly the galactose derivative), were isolated.

Osyritrin, the quercetin glucoside of *Osyris compressa* (*Trans.*, 1897, **71**, 1131), has at 130° the formula $2C_{27}H_{28}O_{16},H_2O$, and not $C_{27}H_{30}O_{17}$, as previously stated. Air dried, it contains $3H_2O$, and is anhydrous at 160°. Violaquercitrin (Mandelin, *Jahres.*, 1883, 1369), present in the *Viola tricolor*, has at 160° the formula $C_{27}H_{28}O_{16}$, and not $C_{42}H_{42}O_{24}$ ($=C_{27}H_{26}O_{15}$) there given. Air dried, it contains $3H_2O$, and is identical with osyritrin.

61. "Preparation of orthodimethoxybenzoin, and a new method of preparing salicylaldehyde methyl ether." By J. C. Irvine, B.Sc.

The author described a new and rapid method of obtaining salicylaldehyde methyl ether. A mixture of salicylaldehyde and methyl iodide reacts energetically with dry silver oxide, giving a brown oil, from which a 90 per cent. yield of the pure product is obtained on distillation. The product (b. p. 236—238°) readily solidifies to a crystalline mass melting at 39—40°. On boiling with potassium cyanide in alcoholic solution, this substance may be condensed to *o*-dimethoxybenzoin, a yellow, crystalline solid melting at 101·5°. A notable reaction of this benzoin is its quantitative conversion into the corresponding methyl ether by the action of silver oxide and methyl iodide. This substance crystallises from ether in prisms melting at 59—60°.

62. "Action of hydroxylamine on the anhydrides of bromonitrocamphane." By M. O. Forster.

The compound $C_{10}H_{17}O_2N_2Br$, obtained by the action of hydroxylamine on the anhydrides of 1 : 1-bromonitrocamphane, crystallises from alcohol in rectangular plates and melts at 197°; it reduces ferric chloride and ammoniacal silver nitrate. The *hydrochloride*, *sulphate*, *picrate*, *platinichloride*, and the *carbamide* and *benzoyl* derivatives are well-defined. When nitrous acid acts on the substance, the anhydride melting at 240° is regenerated, and potassium permanganate oxidises it to the compound $C_{10}H_{14}O_2NBr$.

The compound $C_{10}H_{16}O_2N_2$, produced by the action of aqueous sodium hydroxide on the foregoing hydroxylamino-derivative, crystallises in rhomboidal plates and melts at 208°; the *picrate* and *platinichloride* are well-defined.

63. "On the estimation of cocaine and on di-iodo-cocaine hydriodide." By W. Garsed and J. N. Collie, F.R.S.

The object of this research was to find a method for the fairly accurate estimation of cocaine in small quantity.

The estimation of cocaine in presence of cinnamyl cocaine and isatropyl cocaine, and other substances, with which it is associated in coca leaves has not been attempted, the method only dealing with the estimation of cocaine when free or mixed with benzoyl ecgonine and ecgonine, the products of hydrolysis of pure cocaine. When a solution of cocaine in the form of a salt containing about 1 per cent. of cocaine base is titrated by adding excess of decinormal iodine solution till the supernatant liquid contains excess of iodine, a precipitate of di-iodo-cocaine hydriodide, $C_{17}H_{21}NO_4HII_2$, is formed. The excess of iodine in solution can then be estimated by a decinormal sodium thiosulphate solution. The precipitated di-iodo-compound can be collected and weighed, or the cocaine estimated by the amount of iodine used. Any cocaine salt can be used since the potassium iodide in the solution reacts with the salt, producing the iodide. Di-iodo-cocaine hydriodide is a remarkably stable and crystalline compound, crystallising in large, glistening crystals of constant composition.

Cocaine can be estimated in presence of ecgonine, as ecgonine forms a soluble iodo-compound.

Benzoyl ecgonine, however, interferes to a considerable extent with the estimation of cocaine. Making use of the fact that both benzoyl ecgonine and ecgonine are insoluble in ether or light petroleum, a separation can be effected, as cocaine is soluble in both these solvents. The extracted cocaine can then be weighed directly or titrated with iodine.

64. "Note on acetonylacetone." By T. Gray.

The density (0·973) and refractive index (1·4232) of acetonylacetone, purified by conversion into the bisulphite compound, $C_6H_{10}O_2,2NaHSO_3+H_2O$, and regeneration therefrom, were determined, and the molecular refraction $\mathfrak{M}_D = 29{\cdot}85$ found to agree with the value required by the "keto"-formula. Attention was directed to the readiness with which acetonylacetone is resinified by alkalis, by concentrated sulphuric acid and by gaseous hydrochloric acid.

65. "Condensation of acetonylacetone with hydrazine hydrate." By T. Gray.

The products of the interaction of acetonylacetone and hydrazine hydrate were described. Condensation in molecular proportions results in the formation of a base, $C_{12}H_{20}N_4$, b. p. 157—158° at 13 mm. which readily oxidises in air; it forms a hydrochloride, $C_{12}H_{20}N_4,2HCl$, and a chloroplatinate, $C_{12}H_{20}N_4,H_2PtCl_6$. The product of the reaction of the ketone with excess of hydrazine hydrate is a white, crystalline substance having the formula $C_{12}H_{24}N_6$, m. p. 130—132°. The substance gradually undergoes decomposition at the ordinary temperature, is a powerful reducing agent, and is readily decomposed by dilute acids with formation of hydrazine salts.

66. "Preparation of synthetical glucosides." By H. Ryan, M.A., D.Sc., and W. S. Mills, M.A.

Acetochlorogalactose was obtained as a faint yellow, semi-solid syrup slowly soluble in cold alcohol, hot ligroin, ether and chloroform, scarcely soluble in cold ligroin, by the action of acetyl chloride on well-dried galactose in a dry, cooled, sealed tube. It was extracted with chloroform, washed with ice water and cold sodium carbonate solution; the chloroform solution, dried with calcium chloride and evaporated in a vacuum, left acetochlorogalactose.

By the action of *α*-naphthol and potassium hydroxide on acetochlorogalactose in alcoholic solution, *α-naphthylgalactoside* ($C_6H_{11}O_5\cdot O\cdot C_{10}H_7$) was obtained as rectangular plates soluble in hot alcohol and hot water, slightly soluble in cold water, insoluble in ether, chloroform, benzene and ethyl acetate. It reduces Fehling's solution after inversion by hot dilute sulphuric acid. The galactoside does not dissolve in dilute potash, and melts at 202—203°.

m-Cresylglucoside was obtained from acetochloroglucose and *m*-cresol in alkaline solution as long, silky, branching needles, scarcely soluble in benzene, chloroform, ethyl acetate, and carbon bisulphide, soluble in cold water and alcohol, readily soluble in hot water and alcohol. It reduces Fehling's solution only after hydrolysis by dilute sulphuric acid, m. p. 167·5—168·5°.

The carvacryl glucoside already prepared from acetochloroglucose was obtained from carvacrol potash and acetobromoglucose prepared by the method of Königs.

67. "The influence of cane sugar on the conductivities of solutions of potassium chloride, hydrogen chloride, and potassium hydroxide; with evidence of salt formation in the last case." By C. J. Martin and O. Masson.

Sugar-solution is generally considered to be a non-electrolyte, but in view of the fact that saccharates exist, it may more probably be viewed as a very slightly ionised acid. To test this point, the conductivities of solutions of hydrogen chloride and of potassium chloride containing varying amounts of sugar were determined, and it was found that the conductivity did not appreciably differ from that of aqueous solutions of these compounds, except in so far as the viscosity of the sugar solution had to be allowed for. On the other hand, when sodium hydroxide was added to sugar solutions of different strengths, it was obvious that the sugar took part in the conduction, and this is attributable to the formation of sodium saccharate, which, like other salts, is largely ionised in dilute solution. The conductivity, even in this last case, was of course influenced by the viscosity of the sugar solution, but even after allowing for this, the proof of ionisation was unmistakable.

68. "The aluminium-mercury couple. Part III. Chlorination of aromatic hydrocarbons in presence of the couple. The constitution of the dichlorotoluenes." By J. B. Cohen and H. D. Dakin.

The authors have continued their investigation on the action of the aluminium-mercury couple as a halogen carrier in the preparation of the chlorine derivatives of the aromatic hydrocarbons. They have obtained in this way a series of chlorobenzenes from mono- to hexa-chlorobenzene as well as mono-, di-, and tri-chlorotoluenes. Their work was, however, chiefly devoted to the identification of the dichlorotoluenes formed by this process, a subject which has been under investigation since 1866, with very conflicting results. By careful fractional crystallisation of the following solid derivatives of the mixed dichlorotoluenes, nitro-, dinitro-, sulphonic acids and salts, sulphonic chlorides and amides, and the dichlorobenzoic acids obtained by oxidation, and by a comparison of these with the same derivatives of the six isomeric dichlorotoluenes which they have prepared in a pure state, the authors have now proved that four, namely, ($CH_3 = 1$), 1 : 2 : 3, 1 : 2 : 4, 1 : 2 : 6, and 1 : 3 : 4 and very probably 1 : 2 : 5 dichlorotoluenes are formed in this reaction. The authors propose to investigate the dibromotoluenes in the same manner, as no very satisfactory evidence has been given of the nature of the mixture formed by brominating toluene.

69. "A modification of Gutzeit's test for arsenic." By E. Dowzard.

An apparatus to free the gas from hydrogen sulphide, &c., by washing was described along with a series of experiments, which show that lead acetate solution only absorbs hydrogen sulphide, whilst a 15 per cent. solution of cuprous chloride in hydrochloric acid absorbs hydrogen sulphide, stibine, and phosphine, but has no effect on arsine.

70. "On the chemistry of 'Nerium odorum.'" By R. C. L. Bose, M.B.

In his investigations on the poisonous constituents of *Nerium odorum*, the sweet-scented oleander, two methods of analysis of the roots were employed by the author, namely, that adopted by Greenish (*Pharm. Journ.*, 1881, [iii],11, 873), with certain modifications, and the method of plant analysis of Dragendorff. A third active constituent, besides the two already discovered in the root by Greenish, neriodorein and neriodorin, has thus been discovered, and named *karabin*, from *karabi*, the Bengali name of the plant.

The root gave the following percentages of the different extracts by Dragendorff's method: light petroleum extract, 2·88; ether extract, 1·38; absolute alcoholic extract, 3·40; aqueous extract, 5·81 per cent.

The ether extract was found to contain the *karabin*. This extract was partly soluble in absolute alcohol, giving a clear yellow solution, and on being evaporated to dryness left a brownish-yellow, sticky residue, *karabin*, which on analysis gave numbers corresponding to the formula $C_{21}H_{49}O_6$.

The alcoholic extract contained a substance identified as the neriodorin, and the aqueous extract contained the neriodorein. Neriodorein is readily soluble in water, neriodorin in boiling water only, while *karabin* is insoluble both in cold and boiling water. Neriodorein and neriodorin are insoluble in ether and benzene, but *karabin* dissolves readily in both. The colour reactions with concentrated sulphuric acid are also distinctive.

The author was also able to separate *karabin* by employing the following modification of Greenish's plan of analysis. The acidified aqueous solution of the alcoholic extract of the root was first shaken up with light petroleum, which removed a quantity of a viscid, yellowish, oily substance. After the separation from the light petroleum, the solution was next agitated with ether *instead of chloroform*. The ethereal solution on evaporation left a brownish-yellow residue which gave all the reactions of *karabin*. The acidified fluid was next agitated

with chloroform, which caused the separation of some oily looking globules which floated between the two layers of fluids; these were separated, washed, and evaporated to dryness; the residue gave all the reactions of neriodorein. The chloroform solution was then separated, and on evaporation left a golden-yellow brittle residue which satisfied all the tests for neriodorin.

The author considers that neriodorin is a variety of saponin. Neriodorein is very readily soluble in water, forming a pale yellow solution of neutral reaction which froths considerably on agitation. It has the acrid taste of saponin, and satisfied most of the tests for this widely distributed substance. It also closely resembles, in its behaviour with certain reagents, the variety of saponin described by the author and Warden (*Pharm. Journ.*, 1882, [iii], **12**, 302).

The author believes that both neriodorin and karabin are not glucosides but possess the characters of a resin; neither contains nitrogen.

71. "Change and interaction in organic compounds." By A. Lapworth.

The apparently very general law to which the author has recently endeavoured to draw attention (this vol., p. 2) receives a very simple explanation if it be supposed that isomeric change is due to dissociation and that *the dissociation between two atoms which leads to change in organic compounds exists, in general, only once in the molecule at any instant.* Such a view leads to the $\alpha\gamma$- and $\alpha\beta$-rules, whether the labile group in an isomeric change never leaves the molecule as previously suggested (*Trans.*, 1898. **73**, 448), or whether ionisation occurs, for the above law holds true for weak electrolytes. In the author's opinion, therefore, the cause of change in general in organic compounds is probably to be sought for in a dissociation resembling ionisation, doubtless often in very small amount, a view arrived at independently of Euler (*Ber.*, 1900, **33**, 3202), and Zengelis (*Ber.*, 1901, **34**, 198), who use a similar assumption in order to explain the phenomena of hydrolysis and etherification.

The influence of a catalytic agent might be of very varying character and can only be properly discussed in reference to particular cases. It may not only increase the velocity of change by raising the concentration of ions representing a labile group in isomeric change, or remove certain ions from the sphere of action by converting them into undissociated compounds, a suggestion which has been made by Euler and Zengelis, but, what is of equal importance, it may convert a molecule into an individual possessing the properties of a dissociated group or ion by supplying simpler groups with which it may unite, a process analogous to the formation of a complex ion by union of a simple ion

with a neutral component (compare Abegg and Bödlander, *Zeit. anorg. Chem.*, 1899, 20, 453).

It is to be observed that a molecule may also become a dissociated group by union with a dissociated part of a substance directly concerned in an interaction.

The atom from which a group has been removed will, of course, have an apparent valency of one unit less than that which it has in an undissociated compound; such an atom may be said to be "*subvalent*," or to represent a position of "*subvalency*." Whilst the atoms within a dissociated group will not change their relative positions in any way, the position of "subvalency" may conceivably be altered by a slight readjustment of the mutually attractive forces between the atoms; the removal of a group from one already dissociated does not mean a double dissociation, but the transference of the subvalency (and charge) to that group, and is analogous to the conversion of a complex ion into a simple ion and a neutral component. Perhaps, therefore, the above law should be stated—*No alteration of the relative positions of the atoms in a dissociated group can take place, and as a rule only one position of subvalency exists in such a group at any instant, in other words, it is usually subvalent.*

By means of the conception, the following rule may be deduced for some cases of interaction. If, during a reaction, a group M might be expected to become associated, even momentarily, with an atom R_α in the complex, $\cdot R_\alpha \cdot R_\beta : R_\gamma$, then the product may contain, not only substances with the grouping $R_\alpha M \cdot R_\beta : R_\gamma$, but also, and sometimes exclusively, those with the grouping, $R_\alpha : R_\beta \cdot R_\gamma M$, or their tautomeric forms.

This rule at once gives some reason for the simultaneous formation of *ortho*- and *para*-derivatives when substitution occurs in a benzene mono-derivative, and for the similar but more complicated phenomena in the naphthalene series. Certain equations of considerable interest and importance may also be deduced. For example, if $X \cdot Y + A : B = AX \cdot BY$ is a possible reaction, then, expanding in terms of the rule, we obtain the following possibilities:

$$X \cdot Y + A : B_\alpha \cdot B_\beta : B_\gamma = AX \cdot B_\alpha : B_\beta \cdot B_\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (R)$$

at once recognisable as the form to which so much importance has been attached by Thiele.

$$X \cdot Y_\alpha \cdot Y_\beta : Y_\gamma + A : B = AX \cdot BY_\gamma \cdot Y_\beta : Y_\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S)$$

a form which is not translatable in terms of Thiele's rule. It is probably the basis of the Claisen reaction, the reactions between aldehydes and phenols, or the alkali salts of isonitro-compounds, and the change which occurs when *o*-acetylacetoacetic ester is converted into

diacetylacetic ester by a trace of alkali. Expanding both B and Y, we obtain the form

$$X{\cdot}Y_{\alpha}{\cdot}Y_{\beta}{:}Y_{\gamma} + A{:}B_{\alpha}{\cdot}B_{\beta}{:}B_{\gamma} = AX{\cdot}B_{\alpha}{:}B_{\beta}{\cdot}B_{\gamma}{\cdot}Y_{\gamma}{\cdot}Y_{\beta}{:}Y_{\alpha} \quad . \quad . \quad . \quad (T)$$

which finds examples in the interactions of ethyl sodio-acetoacetate, malonate, cyanacetate, &c. (*iso*-forms), or $\alpha\beta$-unsaturated esters and ketones. In the above examples, X = K or Na, and $Y_{\alpha} = O$.

72. "The mechanism of the Claisen reaction." By A. Lapworth.

The author takes the following view of this reaction in its simplest form :

(1) A sodium ion unites with the carbonyl group of the ketone or ester to form a subvalent group which then loses a hydrogen ion, $\dot{N}a + O{:}CR^1{\cdot}CH_2R^2 \rightarrow Na{\cdot}O{\cdot}\dot{C}R^1{\cdot}CH_2R^2 \rightarrow Na{\cdot}O{\cdot}CR^1{:}CHR^2 + \dot{H}$. The apparently direct replacement of a hydrogen atom in many esters, ketones, or even hydrocarbons (Thiele, *Ber.*, 1901, **34**, 68) is probably to be ascribed to the same cause; the reaction with hydrocarbons may be represented, $\dot{K} + CR_2{:}CR{\cdot}CHR_2 \rightarrow CR_2K{\cdot}\dot{C}R{\cdot}CHR_2 \rightarrow CR_2K{\cdot}CR{:}CR_2 + \dot{H}$, or, another possible type, $CHR{:}CR_2 + \dot{K} \rightarrow CHRK{\cdot}\dot{C}R_2 \rightarrow CRK{:}CR_2 + \dot{H}$.

(2) The metallic derivative then dissociates, part reacting with a subvalent group—produced by union of a sodium ion with ethyl oxalate, formate, &c.—as roughly represented by equation S (see preceding abstract).

$$Na{\cdot}O{\cdot}CR^1{:}CHR^2 + CR^3(OEt){:}O \rightarrow [\dot{O}{\cdot}CR^1{:}CHR^2 + \dot{C}R^3(OEt){\cdot}ONa] \rightarrow O{:}CR^1{\cdot}CHR^2{\cdot}CR^3(OEt){\cdot}NaO \rightarrow O{:}CR^1{\cdot}CR^2{:}CR^3{\cdot}ONa + HOEt.$$

In the case of ethyl crotonate (*Proc.*, 1900, **16**, 132) the $\alpha\gamma$-rule must be applied a stage farther, $Na{\cdot}O{\cdot}C(OEt){:}\overset{1}{C}H{\cdot}CH{:}CH_2 + O{:}\overset{2}{C}(OEt){\cdot}CO_2Et = Na{\cdot}O{\cdot}C(OEt)(\overset{2}{C}O_2Et){\cdot}CH_2{\cdot}CH{:}CH{\cdot}C(OEt){:}\overset{1}{O} = Na{\cdot}O{\cdot}C(CO_2Et){:}CH{\cdot}CH{:}CH{\cdot}CO_2Et + HOEt.$

Exactly similar changes may be supposed to go on in the case of *o*-nitrotoluene, but here the nitro-group takes the place of the carbonyl group in the above cases. In *p*-nitrotoluene a further extension of the $\alpha\gamma$-rule is involved.

The action of hydrogen chloride in promoting the condensation of aldehydes with ketones, phenols, &c., may be ascribed to a similar series of changes, the hydrogen ions acting perhaps in this way :

(1) $\dot{H} + O{:}C(CH_3){\cdot}CH_3 \rightarrow H{\cdot}O{\cdot}\dot{C}(CH_3){\cdot}CH_3 \rightarrow H{\cdot}O{\cdot}C(CH_3){:}CH_2 + \dot{H}$.

(2) $\dot{H} + O{:}CHPh \rightarrow H{\cdot}O{\cdot}\dot{C}HPh$.

(3) $\dot{O}{\cdot}C(CH_3){:}CH_2 + \dot{C}H(OH)Ph \rightarrow O{:}CMe{\cdot}CH_2{\cdot}CH(OH)Ph \rightarrow O{:}CMe{\cdot}CH{:}CHPh + HOH.$

Further experiments on diethyl oxalocrotonate (*Proc.*, 1900, **16**, 132) have strengthened the belief that it is the γ-oxalo-derivative; it has the normal molecular weight in acetic acid.

γ-Oxalocrotonic acid, $CO_2H\cdot C(OH):CH\cdot CH:CH\cdot CO_2H$, is a strong acid which is sparingly soluble in the ordinary organic media. It melts and decomposes at about 190°, being converted into α-pyrone-α'-carboxylic acid. Its aqueous solution gives an intense black colour with ferric chloride which is not discharged by a large excess of hydrochloric acid.

Preliminary experiments on other αβ-unsaturated esters and ketones indicate that the following substances yield acidic compounds resembling ethyl oxalocrotonate: ethyl dimethylacrylate, ethyl β-chlorocrotonate, phorone, camphorone and benzylidenemesityl oxide. The products, which have as yet been obtained only as oils, give intense black colorations with ferric chloride; they are still under examination.

Ethyl α-methylacrylate, which does not contain the requisite grouping, gives no product of a similar kind, indicating that it is not the mere presence of the group $\cdot CH_2\cdot \dot{C}:\dot{C}$ which is necessary.

73. "A new series of di-mercuri-ammonium salts. Part I." By P. C. Rây, D.Sc.

When a solution of mercuric nitrite is treated with ammonia in slight excess, a di-mercuri-ammonium nitrite of the formula $2NHg_2NO_2,H_2O$ is formed; if this compound be dissolved in hydrochloric acid and the solution evaporated nearly to dryness, a white crystalline salt of the formula $NHg_2Cl,4HCl$ is obtained. Hydrobromic acid also yields the corresponding double bromide $NHg_2Br,4HBr$. Both haloid salts dissolve in water and if the solutions be cautiously treated in the cold with dilute potassium hydroxide, the chloride and bromide, $2NHg_2Cl,H_2O$ and $2NHg_2Br,H_2O$, are formed respectively.

At the next meeting, on Thursday, May 2nd, there will be a ballot for the election of Fellows, and the following paper will be communicated:—

"The synthetical formation of bridged-rings. Part I. Some derivatives of bi*cyclo*pentane." By W. H. Perkin, jun., and J. F. Thorpe.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

The following Candidates have been proposed for election. A ballot will be held on Thursday, May 2, 1901.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Anderson, William Carrick,

2, Florentine Gardens, Hillhead, Glasgow.

Assistant to Professor of Chemistry and Lecturer on Chemistry, Glasgow University. Bachelor of Science, 1894 (Glasgow University). Master of Arts (with Honours in Natural Science), 1893. Doctor of Science (Glasg.), 1899. Papers: "Method of Determining Sp. Gravity of Coke" (*J. Soc. Chem. Ind.*, 1896); "A Contribution to the Chemistry of Coal" (*Phil. Soc. of Glasgow*, 1897); "Some Chemical Properties of Scotch Coal" (*J. Soc. Chem. Ind.*, 1899); "A New Form of Potash Bulb" (*ibid.*, 1899); "The Estimation of Iodine in Presence of Cyanides" (*ibid.*, 1899); "The Chemistry of Coke" (Glasgow: Wm. Hodge & Co., 1899), Simmersbach & Anderson; "The Recovery of Nitrogen in Coal Distillation" (*J. Soc. Chem. Ind.*, 1899); "The Oxidation of Ammonia by Iron Ore" (*ibid.*, 1900).

John Ferguson.	**Matthew A. Parker.**
G. G. Henderson.	**James Robson.**
Thomas Gray.	**James Roberts.**

Blake, George Stanfield,

Purley Lodge, Purley, near Croydon.

Analytical Chemist. Assistant in the Imperial Institute Laboratories. Associate of the Royal School of Mines in Metallurgy. Two years chemist to the Royal Mines of Elba; 18 months chemist with Edward Riley, 2, City Road, E.C.

Wyndham R. Dunstan.	**H. H. Robinson.**
R. L. Jenks.	**Ernest Goulding.**

Thomas Anderson Henry.

Bolton, Edward Richards,

7, Leazes Terrace, Newcastle-on-Tyne.

Managing chemist at Messrs. Trobridge and Co.'s Works, Gateshead-on-Tyne. Studied various branches of Chemistry for the past seven years, both in England and Germany—at King's College, London, and under Prof. Fresenius, also with others in both countries. Am desirous of becoming a member of the Society that I may more closely follow such branches of Science as would aid me in directing my manufactures.

John M. Thomson. Patrick H. Kirkaldy.
Herbert Jackson. J. A. Voelcker.
Charles J. S. Makin.

Bousfield, Edward George Paul,

St. Swithin, Hendon.

Student. Some time at Castner-Kellner Works engaged in Electricity and Chemistry. At present doing research work at Central Technical College, &c.

Henry E. Armstrong. Edward W. Lewis.
Gerald T. Moody. William A. Lethbridge.
T. M. Lowry.

Burgess, Percival James,

Singapore.

M.A. Sidney Sussex College, Cambridge. Government Analyst to the Straits Settlements. Formerly Assistant Demonstrator in the University Chemical Laboratory, Cambridge.

G. D. Liveing. H. J. H. Fenton.
W. J. Sell. W. T. N. Spivey.
F. W. Dootson.

Carter, William,

7, Victoria Street, Clitheroe.

Research Assistant in Organic Chemistry at Blackburn Technical School. Student, Blackburn Technical School, 1895—1897. Student, Royal College Science, 1898—1899, and Owens College, 1899—1900. Now Private Research Assistant to Dr. R. H. Pickard, Blackburn Technical School. Joint author with Dr. Lawrence of papers on "The Hydroxyphenoxy- and Phenylene-di-oxy-acetic acids and derivatives of Ethyl α-methyl-β-phenyl cyan-glutarate."

H. B. Dixon. W. H. Perkin, jun.
Wm. A. Bone. J. F. Thorpe.
W. T. Lawrence. Robert H. Pickard.

Clark, Ernest,

9, Polygon Avenue, Stockport Road, Manchester.

Assistant Lecturer in Chemistry at the Royal Technical Institute, Salford. Student for 4 years at University College, Sheffield; for 1 year at the Owens College, Manchester. Assistant Lecturer in Chemistry for 2 years at Royal Technical Institute, Salford. Published two papers (with Dr. G. Young) on "Naphthyl Carbamides," and "Action of Ammonia and Substituted Ammonias on Acetyl Urethane." B.Sc., London. Late 1851 Exhibition Scholar.

W. Carleton Williams. W. H. Perkin, jun.
George Young. Jas. R. Appleyard.
William H. Oates. *Ernest Witham.*

Cockburn, Thomas Kennedy,

26, Elm Street, Whiteinch, Glasgow.

Analytical Chemist. Student in the Laboratory of Messrs. Tatlock & Thompson, Glasgow. Chemist to the Glasgow Portland Cement Company, Ltd. Assistant Chemist to the Millom and Askam Hæmatite Iron Company, Ltd. Assistant to F. W. Harris, F.C.S., Glasgow Corporation Chemist.

R. R. Tatlock. R. T. Thomson.
Jas. D. Dougall. F. W. Harris.
Horatio Ballantyne.

Coddington, Eustace,

131, St. James's Road, Upper Tooting, London, S.W.

Science Master, King Henry VIII. School, Coventry. Open Scholarship for Natural Science at Downing College, Cambridge. Natural Science Tripos, Part I., 1899, Second Class B.A.

W. J. Sell. W. T. N. Spivey.
Henry Jackson. H. O. Jones.
Matthew Whittam.

Crocker, Walter Stevens,

25, Upper Parliament Street, Liverpool.

Chemist and Under-Brewer, Mersey Brewery, Liverpool. Student at the Royal College of Science, London, 1889—1892, taking the Associateship in Chemistry under Dr. Thorpe, F.R.S. Assistant Lecturer and Demonstrator in Chemistry and Physics, Hartley College, Southampton, 1892—4; Assistant to the Southampton Borough Analyst, 1895. Lecturer in Chemistry, Physics, and Geology, Northcroft, Bath, 1896—8. Science Master (Chem. and Phys.), Grammar

School, Gillingham, Dorset, 1898—1900. Appointed as above, December, 1900.

T. E. Thorpe. W. Palmer Wynne.
Leonard Temple Thorne. *F. J. M. Page.*
H. Brereton Baker.

Dakin, Henry Drysdale,
9, Beech Grove Terrace, Leeds.

Student at the Yorkshire College, Leeds. Over four years with Leeds City and County Analyst; three years Student at the Yorkshire College. Published paper with Dr. Cohen on the "Bromination of Aromatic Compounds" (*Trans.*, 75, 893); also papers on the "Estimation of Zinc" (*Zeitschrift. f. anal. Chem.*, 39, 273) and of "Manganese and Cobalt" (*ibid.*, 784).

Arthur Smithells. H. M. Dawson.
Julius B. Cohen. B. A. Burrell.
Thomas Fairley.

Dubois, Raymond,
Rutherglen, Victoria.

Principal of Viticultural and Œnological College. B.Sc. (Paris). Diplomé, École d'Agriculture de Montpellier. Commissioned by the French Government to study and report on the date palm industry in the Oued Rhir from a scientific and commercial point of view. Published report on date palm industry. Translation of "L'Industrie viticole méridionale," by L. Roos; translation of "Guide ampelographique," by M. Mazade; translation of "Traitement des Vins et leurs Maladies," by Malvezin. Compilations: "Trenching and Subsoiling for American Vines," "Sterilisation of Wines," "Herbaceous Grafting," "The Composition of Natural Wines," a paper read before the Austr. Assoc. for the advancement of science. Delivered many public lectures on diseases of wines, casse in wines, chemistry of wines generally, &c., &c.

C. R. Blackett. H. W. Potts.
A. W. Craig. *Orme Masson.*
Henry C. Jenkins.

Duckworth, William Henry,
87, New Bank Road, Blackburn.

Assistant Lecturer and Demonstrator in Chemistry, Blackburn Municipal Technical School. Also Assistant to Dr. R. H. Pickard. Consulting Chemist and Gas Examiner to the Corporation of Blackburn.

Robert H. Pickard. W. E. Bickerdike.
T. Slater Price. W. B. Hards.
C. Gerland.

Dunstan, Albert Ernest,

24, Lidfield Road, Stoke Newington, N.

A Science Master at Owen's School, Islington. B.Sc. London (Hon.'s Chem. Inter. Sci.). I am desirous of keeping in touch with recent chemical work.

William A. Tilden.	G. T. Morgan.
W. Palmer Wynne.	James C. Philip.
M. O. Forster.	*Chapman Jones.*

Eastick, Samuel Philip,

25, Woodville Road, Ealing.

Chemist and Engineer. Studied as Government Teacher four years at Royal School of Mines and Normal School of Science under Professors Frankland, Huxley, Guthrie, Judd, and others; passed 1st or 2nd class in all subjects. Hold teachers certificates in almost every science under the S. and A. Dept. Studied technical chemistry two years under Prof. Lunge at Zurich. Held appointments as chemist for about six years at Beckton Gas Co., Forbes Abbott and Lennard MacDougal Bros., and Kellner Partington Pulp Co., Ltd. About eight years' experience in foreign countries as Chemical Engineer, &c.

L. J. de Whalley.	Chas. E. Eastick.
B. E. R. Newlands.	*Arthur R. Ling.*
Theo. D. Lichtenstein.	*John Heron.*

Ellis, Hugh Edward,

18, Belmont Road, Aberdeen.

Teacher of Chemistry, School of Pharmacy, Robert Gordon's College, Aberdeen (for the past two and half years); late Demonstrator in Chemistry, Northern College of Pharmacy, Manchester; formerly student of Chemistry at the University College of Wales, Aberystwyth, the Northern College of Pharmacy, &c.; Pharmaceutical Chemist and Member of the Pharmaceutical Society.

Herbert McLeod.	J. F. Tocher.
George Clayton.	H. Lloyd Snape.

F. R. Japp.

Eyre, John Vargas,

26, Bridge Road West, Battersea Park, S.W.

Junior Demonstrator in Chemical Laboratory, and Research Assistant to Professor Meldola, F.R.S., at Finsbury Technical College.

R. Meldola.	Edward W. Lewis.
F. Southerden.	Chas. R. Darling.
Gerald T. Moody.	*William A. Lethbridge.*

Hanley, John, A.I.C.,

4, Guion Road, Litherland, Liverpool.

Analyst, now in the employ of J. Bibby and Sons, Liverpool. Three years Technical Chemist to Bancroft and Co., Limited, Liverpool (oils, fats, soap). Three years Student, University College, Liverpool. Five years working out original processes in a private laboratory. Six months Bacteriology, University College, Liverpool. Two years Senior Chemist with J. Bibby and Sons, Liverpool, establishing above process in oils, fats, soaps, glycerine, stearine, oleine, feeding cake, &c.

T. H. Lloyd. H. B. Stocks.
J. Campbell Brown. Joseph T. Freestone.
George Tate.

Harrison, John Ansted,

47, London Road, Neath, Glamorganshire.

Science Master, the County School, Neath. B.Sc. (Lond.) First Division. Honours in Chemistry and Geology. Associate of the Royal College of Science (Lond.) in the Division of Chemistry. Science Student at Mason College (2 years), and the Royal College of Science (3 years). Author of "First Steps in Earth-knowledge."

William A. Tilden. *W. H. Deering.*
W. Palmer Wynne. *T. H. Dodd.*
Lionel M. Jones. *Oliver Trigger.*

Henley, Francis Robert,

Watford, Rugby.

B.A., Oxford (Honours in Chemistry). Engaged in Study of Chemistry of Brewing.

D. H. Nagel. H. B. Hartley.
A. F. Walden. A. Vernon Harcourt.
S. A. Ionides.

Higgs, Henry Herbert,

26, Anglesey St., Lozells, Birmingham.

Schoolmaster. B.Sc. (Lond.). Five years Assistant Schoolmaster (Science) at King Edward's School, Aston, Birmingham.

T. Francis Rutter. *E. J. Cox.*
William Round. *C. F. Baker.*
Albert H. Turton. *Percy F. Frankland.*

Hyder, Alfred James,

22, Gunton Rd., Upper Clapton, London, N.E.

Teacher of Chemistry. (Inter.) B.Sc. London University and Honours, Inorganic (Practical), of Science and Art Department. I

desire to attend Chemical Society's meetings, to have Journal published by the Society, and use of the Library, as I take much interest in chemical work.

J. T. Hewitt. Edgar S. Barralet.
Frank Dixon. *F. D. Chattaway.*
K. J. P. Orton.

Jemmett, William Henry Coutts,
Tintern, Gap Road, Wimbledon.

Senior Chemistry Master at Owen's School, Islington. 1st Class, Nat. Sci. Tripos, Part I., Cambridge, 1893, Chemistry being one subject of examination. Teacher of Chemistry for over seven years. Desirous of following modern developments in Chemistry.

F. H. Neville. C. T. Heycock.
Holland Crompton. William J. Pope.
Stuart Blofeld.

McKenzie, Alex.,
Jenner Institute, Chelsea Gardens, London, S.W.

Grocers' Company Research Student. M.A., D.Sc. (St. Andrews), Ph.D. (Berlin); Author of "Active and Inactive Phenylalkyloxyacetic Acids" (*Trans.*, 75, 753); "A Contribution to the Chemistry of the Mandelic Acids" (*ibid.*, 75, 964); Inaugural-Dissertation, Berlin, 1901, "I Teil: Ueber eine neue Methode zur Spaltung racemischer Verbindungen in die activen Bestandteile. II Teil: Ueber die Abscheidung von Isobutylcarbinol und Methylaethylcarbincarbinol aus Gährungsamylalkohol." Also conjointly with W. Marckwald, author of several papers in the *Berichte*, 1899, 1900, 1901.

Henry E. Roscoe. Arthur Harden.
G. Druce Lander. Harold G. Colman.
J. H. van't Hoff.

Lewis, Ernest Alfred,
310, Dudley Road, Birmingham.

Analytical Chemist, Assayer, and Metallurgist. 1895, 1896, Student at Mason College, Birmingham; 1897, 1898, Assistant at Muntz's Metal Co., Ld., French Walls, near Birmingham; since 1899, Chemist and Metallurgist to Muntz's Metal Co., Ltd. Published an article on "The Effect of Arsenic on Copper," in *Chemical News*, Jan. 4th, 1901. Have done research work on "The Effect of very Dilute Acids on Metals and Alloys," and "On the Microstructure of Copper, Brass, &c."

Percy F. Frankland. T. Slater Price.
C. F. Baker. T. Goode Joyce.
D. R. Boyd.

Loewenthal, Oscar,
Mill Hill Park, London, W.
Student in Chemistry. Student in Chemistry at the University of Geneva.

C. Graebe.	R. H. Aders.
C. A. Buckmaster.	*W. Pullinger.*
Frank E. Weston.	*J. Wertheimer.*

Mees, Charles Edward Kenneth,
33, St. Saviour's Road, Croydon.
Student in the Chemical Department of University College, London. Passed Intermediate Examination in Science. Reading for B.Sc. (Honours) Examination at the London University.

M. W. Travers.	Edward C. Cyril Baly.
Charles M. Stuart.	Lionel M. Jones.

William Ramsay.

Murphy, Albert John,
Preston House, Leeds.
Consulting Brewing Chemist. Trained for Moravian ministry; late Assistant Master at Stamford Grammar School and Army Coaching School, Sevenoaks. Member of Council of Institutes of Brewing; of Publication Committee of Journal of these Institutes; of Society of Public Analysts; occasional contributor to Scientific Brewing Journals.

Arthur Smithells.	H. M. Dawson.
John Heron.	John Heaton.
Arthur R. Ling.	Alfred C. Chapman.

Neil, Arthur Theodore,
21, South Grove, Highgate, N.
Schoolmaster (Science Master, Sutton Valence School). Honours in the Natural Sciences Tripos, Cambridge; Chief Subject, Chemistry. Science Master, Sutton Valence School. Anxious to follow the progress of Chemistry.

W. J. Sell.	H. J. H. Fenton.
W. T. N. Spivey.	F. W. Dootson.

Henry Jackson.

Neumann, Edgar,
10, Randolph Crescent, Maida Vale, London, W.
At Messrs. Forbes, Abbott, and Lennard's Tar Distillery, Greenwich.

B.A. (Oxon), Ph.D. (Gottingen). The thesis was on the "Isomerism of Fenchene Derivatives."

D. H. Nagel. A. D. Hall.
A. F. Walden. William Ramsay.
A. M. Kellas.

Oldershaw, William,
Market Place, Nottingham.

Chemist. Engaged for upwards of 20 years in Analytical and Manufacturing Chemistry. Reasons for desiring admission to the Society, to attend when special papers or lectures are given; to have access to the Society's Library.

Leonard de Koningh. Will. F. Mawer.
Albert Ivatt. *R. H. Harland.*
W. Watson Will.

Peacock, Arthur,
Smithies Bridge House, Heckmondwike, Yorks.

Assistant Schoolmaster. B.Sc. (Vic. Univ.) Chemistry in Final. Four years in Chemical Laboratory, 2 in Physical Laboratory, and 2 in Geological Laboratory, Yorkshire College. Have taught Chemistry, Physics, and Mechanics, for which I am qualified under Board of Education Regulations.

Arthur Smithells. John McCrae.
Herbert Ingle. Harry M. Dawson.
A. V. C. Fenby. James Foulds.
Julius B. Cohen. T. W. Lockwood.

Robertson, William,
41, Rosenau Road, Battersea Park, S.W.

Science Teacher. Educated at Allan Glen's School, the Glasgow and West of Scotland Technical College, and Royal College of Science, London (Frank Hatton Prize Winner and Associate in Chemistry of First Class, 1896–99). At present demonstrating in Chemistry at the Royal College of Science and Wandsworth Technical Institute.

William A. Tilden. G. T. Morgan.
W. Palmer Wynne. A. Greeves.
M. O. Forster. Thomas Gray.

Robinson, William Hammond,
The Limes, Painswick Rd., Cheltenham.

Schoolmaster. Head of the Public Science Classes affiliated to the Cheltenham Grammar School. M.A. Oxford. First Class Honours in Final Honour School of Natural Science (Chemistry),

1889. Since this date I have been engaged in teaching science, as Univ. Extension Lecturer, and in Secondary and Technical Schools.

William Odling. W. W. Fisher.
V. H. Veley. J. E. Marsh.
John Watts.

Shepperson, William,
"Longfield," Great Missenden, Bucks.

Gentleman. Being interested in the Science and desirous of obtaining the Journal. Specially interested in the Chemistry and Physiology of Fats.

Samuel Rideal. John Attfield.
Otto Hehner. *W. T. Burgess.*
E. G. Clayton. *P. Gerald Sanford.*

Sherratt, Charles Edmund Shaw,
24, Argyll Road, Normacott, Staffs.

School Teacher and Works Analyst. Attended Science Classes at the Wedgwood Institute, Burslem, for 2 years, and the Longton Science Classes for 6 years, gaining many 1st Class Science Certificates, including Honours (Chemistry). Now Analyst to the Chatterley Whitfield Coal and Iron Company.

Edmund M. Rich. Bennett C. Polkinghorne.
George George. *Thos. J. Cheater.*
Geo. W. Burman.

Slefrig, Samuel,
18, Waterloo Road, Shepton Mallet, Som.

Science Master in a Public Secondary School (School of Science). B.Sc. Vict.—took Chemistry in Prelim. Inter. B.Sc. and Final B.Sc. after full 3 years' course in Prac. and Theoret. Chemistry at University College, Liverpool, under Prof. Campbell Brown, D.Sc., F.I.C., F.C.S. Associate, and late Technical Science Scholar (Chem. and Phys.), University College, Victoria University. Teacher of Chemistry for past 3 years in Schools of Science, under Board of Education, and Somerset County Council. Lecturer in Chemistry, Pupil Teacher Centre, Shepton Mallet, Som.

J. Campbell Brown. Charles A. Kohn.
T. Francis Rutter. *Herbert B. Stocks.*
W. Collingwood Williams.

Smith, Henry Ewing,
22, City Road, London, E.C.

Manufacturing Chemist, chiefly of alkaloidal preparations of opium, morphia, codeia, &c. Member (by examination) of the Pharmaceu-

tical Society of Great Britain. Studied Chemistry under Professor Jamieson at the Technical College, Glasgow; then under Professor W. H. Perkin at Heriot-Watt College, Edinburgh; then under Professor Weber at Zurich for analytical work and investigation of alkaloids, and research thereon of a synthetic nature. Now partner in the firm of T. and H. Smith and Co., Manufacturing Chemists Edinburgh and London.

Paul Thomas White.	*David Howard.*
Thos. Tyrer.	*D. Lloyd Howard.*
Alfred Gordon Salamon.	*Reginald G. Halstead.*

Smith, James,

14, Mersey Road, Aigburth, Liverpool.

Analytical Chemist. Engaged for seven years in general analytical work in the laboratory of Mr. G. Watson Gray, F.I.C., also studied Organic and Inorganic Chemistry under Dr. George Tate, F.I.C., F.C.S.

George Tate.	Saml. Banner.
Thomas J. Roberts.	*Charles A. Kohn.*

C. J. Head.

Stell, Samuel Fenton,

25, Henry Street, Keighley.

Teacher of Chemistry. Fifteen years Lecturer and Demonstrator in Chemistry, Day and Evening Classes, Technical College, Bradford.

Walter M. Gardner.	A. B. Knaggs.
A. William Gilbody.	S. F. Dufton.

G. W. Slatter.

Taylor, William Henry,

19, Shafton Road, Victoria Park Road, N.E.

Chemist to Messrs. Burroughs, Wellcome and Co. A.I.C. Certificated Student of Finsbury Technical College. For 1 year at University College, London. Eighteen months in present position. Working for Final B.Sc.

Raphael Meldola.	Francis H. Carr.
William Ramsay.	E. F. Harrison.
Harold Picton.	*Frederick B. Power.*

Tozer, Herbert Ackerman,

113, Stepney Green, London, E.

Schoolmaster, London School Board. Bachelor of Arts, Univ. of London. I hold Advanced Certificate in Chemistry of Science and Art Department, also in Mathematics—three—and in Magnetism and Electricity. Am a Candidate for the B.Sc. Degree (Inter.) of

London University. Have been a student for two terms at University Tutorial College, Red Lion Square, under J. W. Shepherd, Esq., B.Sc., first in 1st Class Honours in Chemistry, and E. Catchpool, Esq., B.Sc., 1st Class Honours in Physics. I take a great interest in the progress of Chemical Science, and therefore wish to become a Fellow of the Chem. Soc. and to read its publications.

J. E. Johnson. *T. H. Dodd.*
R. J. Redding. *W. H. Deering.*
J. C. Aylan. *Oliver Trigger.*

Welch, George Edward,

88, Caledonian Road, Leeds.

Science Master. B.Sc., London. Bracketed 1st in 1st Class Honours Prac. Chem., South Kensington. Six and a half years Teacher of Chem. at Bablake School, Coventry. Six years Teacher of Chem. and Physics, Middle Class School, Leeds.

William G. Boul. E. J. Cox.
Thomas Turner. Julius B. Cohen.
Reginald B. Brown.

Wylie, Adam Storer,

93, Manchester Street, Oldham.

Analyst at the Oldham Corporation Sewage Works. Have been employed as Analyst on the Oldham Corporation Sewage Works during the past four years, and have had sole control of between four and five acres of bacteria beds (at present, I believe, the largest area in England). Issued report to the Corporation on the purification of sewage and working of bacteria beds in 1900.

Francis Jones. Frank Scudder.
Percy F. Frankland. Robert Pettigrew.
Gilbert J. Fowler. *W. H. Perkin.*

The following Certificate was authorised by Council under bye-law I (3):

Verteuil, Joseph de,

Clarence Street, Port of Spain, Trinidad, B.W.I.

Assistant Analyst, Government Laboratory, Trinidad. Student, St. Mary's College, Trinidad, 1½ years; Student, Stoneyhurst College, England, 5 years; Student, Institut Beauvais, France, 3 years. Obtained Diploma, "Ingénieur Agricole," Institut Beauvais. Chemist at Orange Grove Sugar Factory, 1 year; Chemist at Esperanza Sugar Factory, 1 year; Assistant Analyst, Government Laboratory, Trinidad, 1 year.

P. Carmody.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY

Issued 9/5/1901

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 237.

May 2nd, 1901. Professor EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

Messrs. Storr and Talbot were formally admitted Fellows of the Society.

The following certificates were read for the first time: Ormsby Gore Adams, Stawell, Victoria; Joseph Samuel Bridges, 45, Thistlewaite Road, Clapton, N.E.; Adolf Ludwig Ferdinand Lehmann, Bangalore, Mysore, India; William Lowson, 83, Kyrle Road, Clapham Common, S.W.; James Bertram Russell, 356, Padiham Road, Burnley; Thomas Sandford, 2, Market Place, Ulverston; Samuel Edward Sheppard, Ravensmere, Bromley Road, Catford, S.E.; Andrew Biggam Smith, Queenstown, Cape Colony; George William Gerald Tatam, Mercers' Hall, Cheapside, E.C.; James Whittle, 30, Bridge Street, Morpeth.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. William C. Anderson, M.A., D.Sc.; George Stanfield Blake; Edward Richards Bolton; Edward G. P. Bousfield; Percival J. Burgess, M.A.; William Carter; Ernest Clark, B.Sc.; Thomas Kennedy Cockburn; Eustace Coddington, B.A.; Walter Stevens Crocker; Henry Drysdale Dakin; Raymond Dubois, B.Sc.; William Henry Duckworth; Albert Ernest Dunstan, B.Sc.; Samuel Philip Eastick; Hugh Edward Ellis; John Vargas Eyre; John Hanley; John A. Harrison, B.Sc.; Francis R. Henley, B.A.; Henry Herbert Higgs, B.Sc.; Alfred James Hyder; William

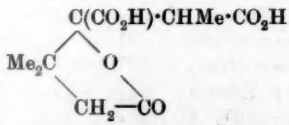
Henry C. Jemmett, B.A.; Ernest Alfred Lewis; Oscar Loewenthal; Alex. McKenzie, M.A., Ph.D., D.Sc.; Charles Edward Kenneth Mees; Albert John Murphy; Arthur Theodore Neil, B.A.; Edgar Neumann, B.A., Ph.D.; William Oldershaw; Arthur Peacock, B.Sc.; William Robertson; William Hammond Robinson, M.A.; William Shepperson; C. Edmund Shaw Sherratt; Samuel Slefrig, B.Sc.; Henry Ewing Smith; James Smith; Samuel Fenton Stell; William Henry Taylor; Herbert Ackerman Tozer, B.A.; Joseph De Verteuil; George Edward Welch, B.Sc.; Adam Storer Wylie.

Professor ARMSTRONG requested that the abstract of Professor Perkin's paper might be read, and suggested that it might be desirable to arrange for accounts to be given by persons specially selected of the work of authors who were unable to be present in person.

Of the following papers, those marked * were read.

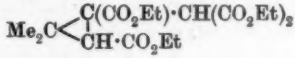
*74. "The synthetical formation of bridged-rings. Part I. Some derivatives of bicyclopentane." By W. H. Perkin, jun., and J. F. Thorpe.

In a paper recently published, Baeyer (*Ber.*, 1901, **33**, 3771) has developed a system of nomenclature for bridged-rings and their derivatives. According to this system, the hydrocarbon $CH_2<\begin{matrix}CH\cdot CH_2\\ |\\ CH\cdot CH_2\end{matrix}$ is named *bicyclopentane*, and the acid $Me_2C<\begin{matrix}C(CO_2H)\cdot CMe\cdot CO_2H\\ |\quad\quad\quad\quad|\\ CH\text{——}CO\end{matrix}$ previously described (*Proc.*, 1900, **16**, 151) is therefore *trimethylketo-bicyclopentanedicarboxylic acid*. It has already been stated that this acid, when digested with potash, is converted into an acid melting at 237°, and it has since been found that the latter yields an anhydride (m. p. 96°) which on distillation is converted into the anhydride (m. p. 131°) of an isomeric acid melting at 181°. Careful investigation has shown that these acids, which are evidently stereoisomeric, are not furfuran derivatives, as was at first supposed, but are *lactones* of *trimethylhydroxybutanetricarboxylic acid*,

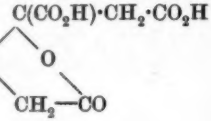


disruption of the whole bicyclopentane ring having taken place during

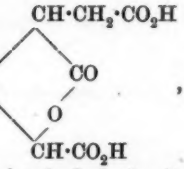
their formation. A somewhat similar decomposition is shown by *ethyl dimethyldicarboxytrimethylenemalonate,*



(*loc. cit.*, p. 149), which on hydrolysis with alcoholic potash yields two acids melting at 187° (not 176° as previously stated) and 158°. These acids have now been shown to be the *lactones* of the two isomeric *dimethylhydroxybutanetricarboxylic acids,*

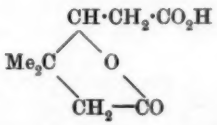


and

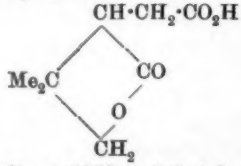


, the trimethylene ring having been broken during hydrolysis; but unfortunately so far it has not been possible to decide which formula belongs to the former and which to the latter of the two acids.

Both acids on heating lose carbon dioxide, and are converted into the *lactones* of two isomeric *dimethylhydroxybutanedicarboxylic acids* probably

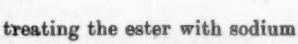


and



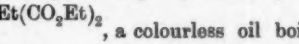
that from the acid of melting point 187° melts at 108°, and that from the acid of melting point 158° at 154°.

During the investigation of the bicyclopentane derivatives, it became necessary to prove conclusively that ethyl dimethyldicarboxytrimethylenemalonate really had the constitution assigned to it above, and that it was not a tetramethylene derivative of the formula



, which was the only other possibility.

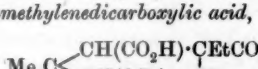
This was done by treating the ester with sodium ethylate and ethyl iodide, when it yielded *ethyl dimethylethyldicarboxytrimethylenemalonate,*



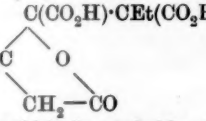
, a colourless oil boiling at 230—232° (30 mm.). The formation of this ethyl derivative shows that the

original ester must have contained a hydrogen atom replaceable by sodium, and the tetramethylene formula given above is therefore excluded.

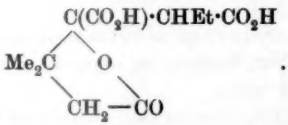
When this ethyl substitution product is digested with alcoholic potash, it yields a dibasic acid (m. p. 175°) which is probably *dimethylethylethoxyketopentamethylenedicarboxylic acid*,



and there is formed, at the same time, a tribasic lactonic acid melting at 193°, which is probably the *lactone* of *dimethylethylhydroxybutane-tetracarboxylic acid*,



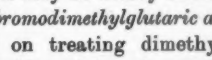
, and a dibasic lactonic acid melting at 213°, which is probably the *trans*-modification of *dimethylethylhydroxybutanetricarboxylic acid*,



The corresponding *cis*-modification, which is obtained by the action of hydrochloric acid on the dimethylethylethoxyketopentamethylenedicarboxylic acid mentioned above, melts at 144°, and gives an anhydride melting at 168°.

The ease with which disruption of the trimethylene ring takes place in the formation of these lactones is very remarkable; the only other similar case which is known is that described by Buchner and Witter (*Ber.*, 1894, **27**, 871).

During the course of the investigation of the bicyclopentane derivatives, some interesting derivatives of *ββ-dimethylglutaric acid*, $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$, have been prepared and examined, and the results may be briefly summarised as follows:—

aa_1-Dibromodimethylglutaric acid, $CO_2H{\cdot}CHBr{\cdot}CMe_2{\cdot}CHBr{\cdot}CO_2H$, is obtained on treating dimethylglutaric anhydride with phosphorus pentachloride and bromine and digesting the product with anhydrous formic acid; it melts at 187—189°, and when treated with pyridine or boiled with water it yields the lactone of *α-bromo-a_1-hydroxydimethylglutaric acid*,  . This melts at 169—170°, gives an ethyl ester boiling at 201° (45 mm.), and is characterised by the great stability of its bromine atom which is not removed even by

boiling with silver nitrate and nitric acid. Strong potash, however, converts it into the *lactone* of *$\alpha\alpha_1$-dihydroxydimethylglutaric acid*, $Me_2C<\begin{matrix}CH(OH)—CO\\ CH(CO_2H)\cdot O\end{matrix}$, which melts at 142°.

During the bromination of dimethylglutaric acid, a small quantity of *$\alpha\alpha$-dibromodimethylglutaric acid*, $CO_2H\cdot CBr_2\cdot CMe_2\cdot CH_2\cdot CO_2H$, is formed, and this, on boiling with sodium carbonate, yields *$\alpha\alpha$-dihydroxydimethylglutaric acid*, $CO_2H\cdot C(OH)_2\cdot CMe_2\cdot CH_2\cdot CO_2H$, which melts at 84° and behaves in many of its reactions as the keto-acid, $CO_2H\cdot CO\cdot CMe_2\cdot CH_2\cdot CO_2H$, containing 1 molecule of water less. Thus it combines with *o*-toluylenediamine, and on reduction with sodium amalgam is converted into the lactone of *α-hydroxydimethylglutaric acid*, $\begin{matrix}CO_2H\cdot CH\cdot CMe_2\cdot CH_2\\ O———CO\end{matrix}$, which melts at 112°, and has already been described (*Trans.*, 1899, **75**, 56).

***75. "Lead silicates in relation to pottery manufacture." By T. E. Thorpe, C.B., F.R.S., and C. Simmonds, B.Sc.**

As is well known, the use of oxides and basic carbonates of lead in glazes employed by potters is attended with danger to the health of the workpeople on account of the ready solubility of these compounds in the acids of the animal organism. Attention was drawn to the fact that lead silicates or boro-silicates, or complex silicates of lead and other metals, can be used instead of the oxides or carbonates as a means of introducing lead into the glaze. On the Continent this use of lead silicates is far more common than in England, and it is generally recognised that their employment has greatly tended to minimise the risk of lead-poisoning. This is due to the fact that the lead silicates used in the continental factories are of a high degree of insolubility so far as the lead is concerned.

On examining a number of lead silicates used or proposed for use in England, it was found that many were attacked by dilute acids practically to the same extent as the oxides or carbonates. That is, they yielded the whole, or nearly the whole, of their lead to the action of acids comparable with the acids found in the human system—such as, for example, the hydrochloric acid of the gastric juice. Other specimens were more resistant, but still yielded a large proportion of their lead. On the other hand, the specimens obtained from the Continent, as well as many which have recently been produced by English manufacturers, gave up only small quantities of lead when tested under the special conditions described.

A large number of specimens was therefore analysed in order to

ascertain, if possible, to what variations in chemical composition these differences of behaviour were due.

The condition on which the insolubility of the lead depends was found to be, primarily, the existence of a certain ratio between the whole of the base-oxides on the one hand, and the whole of the acid-oxides on the other. This becomes eventually referable to the hypothetical silicic acids from which the silicates may be considered to be derived. For working purposes, the relation may be more simply expressed as

$$\frac{\text{sum of percentages of base oxides, expressed as PbO}}{\text{sum of percentages of acid-oxides, expressed as } SiO_2},$$

or, alternatively, as

$$\frac{\text{number of acid molecules}}{\text{number of base molecules}},$$

the latter ratio being obtained by dividing the percentage of each oxide by its molecular weight, and then dividing the sum of the quotients for the acid-oxides by the sum of the quotients for the base-oxides.

Provided the ratio falls within certain definite limits, the amount of lead extracted under the prescribed conditions is always small. It does not depend upon the quantity of lead in the silicate, which may have any value up to 50 or 55 per cent. The other bases usually present (lime, alumina, and alkalis) may also vary considerably, replacing one another, and also the lead oxide, within very wide limits without prejudice to the insolubility of the lead.

Analyses and formulæ of a number of silicates were given, together with tables showing the dependence of the solubility of the lead in the silicates upon the ratios mentioned above.

Discussion.

Mr. F. J. Lloyd asked whether experiments had been made using smaller quantities of solution than 1000 parts to 1 part of substance. The acid present in 1000 c.c. would be about seven times as much as that required to dissolve 1 gram of lead oxide. The conditions which influenced the solubility of substances in dilute acid solutions were of especial interest to agricultural chemists. He had found in some experiments that the volume of solution employed appeared to materially affect the solubility, and wished to know whether the authors had had a similar experience during their investigation.

Prof. Tilden enquired whether the authors had paid special attention to the degree of fineness of the powders submitted to the action of the acid. Some facts had already been published which seemed to show that the apparent solubility of a frit was seriously influenced by the

amount of trituration to which the substance had been subjected before bringing it into contact with the acid.

Professor CLOWES said it would be of interest to know if the solvent action of acids other than hydrochloric acid had been tried, and with what results. He also asked whether the method of testing finished articles purporting to be covered with leadless glaze, by exposing them to the action of dilute hydrochloric acid for some time and examining the solution for the presence of lead, was satisfactory, and what were the best conditions for applying such a test.

Mr. ELWORTHY asked whether the authors had estimated the solubility of the frits or glazes in salt solutions, as they were much more likely to come into contact with salt solution than with free hydrochloric acid, especially during the preparation of food, and whether the lead dissolved from the frit existed in the solution as chloride or as a soluble silicate.

Prof. CARMODY asked whether any comparisons had been made between the amount of lead oxide soluble in the frits before and after their application.

Mr. SIMMONDS, in reply, stated that an excess of acid was necessary, for otherwise misleading results were obtained; this was due to the curious fact that certain kinds of lead silicate reacted with a neutral solution of lead chloride and removed the lead from solution, probably as an insoluble oxychloride. The volume of acid selected must be sufficiently great to ensure that there should be no very considerable weakening of its strength by the action of the various acid-neutralising constituents, of which, it should be borne in mind, there might be several besides the lead.

As regards fineness of subdivision, some of the specimens were sent ready ground, and were stated by the manufacturers to be in the condition in which they were to be used for glazing pottery ware; these were tested as received. The other specimens were ground to an impalpable powder in an agate mortar. Various solvents had been experimented with—for example, lactic and acetic acids—but the results threw no greater light on the subject than those obtained with hydrochloric acid; consequently, the experiments were not persisted in. Salt solution had not been tried. He did not know whether testing the glaze on table ware with hydrochloric acid had been suggested, but in Germany there was a provision that such ware should not give up lead when boiled for half an hour with 4 per cent. acetic acid.

With reference to the state in which the lead existed when dissolved from a silicate, whether as a lead silicate or as lead chloride, complete analyses of several of the solutions had been made, and some small quantity of silica was always present. The lead, or a part of it, may therefore, perhaps, have dissolved as a basic silicate.

76. "The preparation and properties of 2 : 6-dibromo-4-nitrosophenol." By M. O. Forster and W. Robertson.

2 : 6-Dibromo-4-nitrosophenol is produced by the action of potassium hypobromite on *p*-nitrosophenol dissolved in potassium hydroxide solution (compare Fischer and Hepp, *Ber.*, 1888, **21**, 674); the *potassium*, *acetyl*, and *benzoyl* derivatives are well defined. Dilute nitric acid oxidises the substance to 2 : 6-dibromo-4-nitrophenol, but the concentrated acid converts it into 2-bromo-4 : 6-dinitrophenol. Tin and hydrochloric acid reduce 2 : 6-dibromo-4-nitrosophenol to 2 : 6-dibromo-4-aminophenol, of which the *benzoyl* derivative is well defined.

77. "The chlorination of toluene." By W. P. Wynne.

In consequence of the publication of an abstract of a paper by Cohen and Dakin (p. 91), the author wishes to state that he has been, and is, engaged in a study of the chloro-derivatives obtained in chlorinating toluene under Seelig's conditions (*Trans.*, 1892, **61**, 1051). The six dichlorotoluenes, and their sulphonic acids, chlorides, and amides, to which Cohen and Dakin refer, were prepared and examined in this connection (*loc. cit.*, p. 1042; Wynne and Greeves, *Proc.*, 1895, **11**, 151). Moreover, the 2 : 5-dichlorotoluene, which these authors state is very probably formed in presence of the mercury-aluminium couple, has been recognised as present in considerable quantity in the mixture of dichlorotoluenes obtained by Seelig's method.

ERRATA.

Page	Line	
94	18	*after* "place" *insert* "by further dissociation."
94	20	*for* "subvalent" *read* "subunivalent."

At the next ordinary meeting, on Thursday, May 16th, the following papers will be communicated :—

"The nutrition of yeast. Part III." By A. L. Stern, D.Sc.

"Derivatives of methylfurfural." By H. J. H. Fenton and Miss Mildred Gostling.

"The preparation and optical inversion of optically active nitrogen compounds; dextro- and lævo-α-benzylphenylallylmethylammonium salts." By W. J. Pope and A. W. Harvey.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 31/5/1901

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 238.

Extraordinary General Meeting, May 15th, 1901. Professor EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

The PRESIDENT stated that this Meeting had been convened in accordance with a requisition, signed by 66 Fellows of the Society, to consider the decision of the Council to hold the Ordinary Meetings of the Society during the ensuing session on Wednesdays at 5.30 p.m.

After a discussion in which, amongst others, the following Fellows took part: Dr. Lewkowitsch, Dr. Moody, Mr. A. G. Bloxam, Mr. Cassal, Dr. Armstrong, Mr. Hehner, Mr. Tyrer, Mr. Pakes, Prof. Tilden, Prof. Ramsay, Dr. Crossley, Dr. Forster, Prof. Dewar, and Mr. F. J. Lloyd,

Dr. ARMSTRONG moved and Mr. HEHNER seconded the following resolution:—

"That in the opinion of this Meeting the change proposed in the day and hour of Meeting will prevent the attendance of a large proportion of the junior and other Fellows who have hitherto been regular attendants; that the said change is contrary to the best interests of the Society, and that it is desirable that the question be reconsidered by the Council."

The resolution was declared by the President to be carried. The numbers being asked for, a division was taken, with the following result:—For the resolution, 92; against, 3. A certain number of Fellows abstained from voting.

May 16th, 1901. Professor EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

Messrs. McKenzie, Ferguson, Woodbridge, Robertson, Jennings, Dodd, Neil, Mees, Wayland, and Dixon were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Hubert Haigh Barker, 3, Waverley Place, St. John's Wood, N.W.; George Dean, 2, Scriven Grove, Knaresborough; Thomas Henry James Eling, 32, Hill Top Avenue, Shepherd's Lane, Leeds; Edward Kenneth Hanson, Hadley Wood, N.; Frederick Thomas Harry, 106, Sandmere Road, Clapham, S.W.; Edward Horton, 8, Orford Street, Chelsea, S.W.; Christopher George Kiddell, 24, Queen's Gardens, Muswell Hill, N.; Robert Tabor Lattey, Trinity College, Oxford; F. G. Macdonald, Government Laboratory, Durban; Frank Oram, Market Place, Romsey; John Edward Purvis, University Chemical Laboratory, Cambridge; Gerald Theodore Sylvester Sichel, R.N. Hospital, Haslar, Gosport; Duncan Randolph Wilson, Magdalen College, Oxford.

The PRESIDENT read the resolution passed at the Extraordinary General Meeting (*see* p. 117) which he stated had been that afternoon brought before the Council, by whom it was being carefully considered.

Dr. ARMSTRONG, referring to the ruling given by the President at the previous meeting that a paper read in the absence of the author could not be discussed, drew attention to Bye-law XIV, and contended that this bye-law expressly provided that every paper communicated to the Society should be open to discussion. He stated that during the whole course of his experience, extending over 30 years, it had always been the practice of the Society, when the occasion arose, to discuss papers read in the absence of their authors.

Dr. PERKIN, in reply to a question by Dr. Armstrong, said that in the past papers had often been discussed in the absence of their authors.

Dr. DIVERS said that having been resident in Japan when most of his papers were sent to the Society, he had always been willing that they should be discussed.

Prof. DUNSTAN pointed out that Bye-law XIV evidently supposed that authors would be present to read their papers, and its directions could not be literally followed at the present time. In these matters, however, the Bye-law gave large discretion to the chairman.

Mr. W. P. BLOXAM asked whether it was within the power of the President to closure or prevent discussion on any paper read to the Society.

The PRESIDENT replied that as a general rule he should not think of doing so.

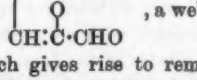
Mr. BLOXAM remarked that probably Dr. Armstrong would recollect when he read a paper on ammonium sulphides, Dr. Armstrong, as President, had prevented any discussion whatever on that paper.

The PRESIDENT considered that the Bye-law read by Dr. Armstrong assumed the presence of the author at the meeting. Criticism on a mere abstract in the author's absence, and without his assent, seemed contrary to the fair general principle which governed most public meetings. On the other hand, he saw no objection to questions relating to points of nomenclature or detail which could be elucidated by reference to the original paper, should the latter be available at the time.

Dr. ARMSTRONG said that such being the President's opinion, and as he could not accept the ruling as correct, it would be necessary for him to raise the question again elsewhere.

Of the following papers, those marked * were read.

***78. "Derivatives of methylfurfural." By H. J. H. Fenton and Miss M. Gostling.**

The authors have already (*Trans.*, 1898, **73**, 554; 1899, **75**, 423; 1901, **79**, 361) described the isolation, properties, and constitution of bromomethylfurfural,  , a well defined, crystalline substance melting at 60° which gives rise to remarkable colour reactions. Because of the interest which attaches to this compound owing to its relations with the carbohydrates and the bearing of its formation on questions in plant physiology, it was considered desirable to make a further study of the compound and its derivatives. The following new compounds were described:

Chloromethylfurfural, m. p. 36—37°; *acetoxy*-derivative, m. p. 55°; *benzoxy*-derivative, m. p. 56—57°; *difurfuryl-ethane-dialdehyde*, m. p. 119—120°; with its corresponding *dihydrazone*, m. p. 179—181°; *dicarboxylic acid*, m. p. 267—269°; and *dioxime*, m. p. 182°. A very simple method of obtaining pure methylfurfural was also described.

DISCUSSION.

Mr. W. J. POPE asked whether bromomethylfurfural, which contains a bromine atom and an ethereal oxygen atom attached to adjacent carbon atoms, was capable of condensing with alkyl sulphides

or tertiary amines to yield sulphonium or quaternary ammonium derivatives.

Mr. FENTON, in reply, said that both the chloro- and the bromo-derivatives of methylfurfural readily interacted with various amines.

***79. "Optically active nitrogen compounds and their bearing on the valency of nitrogen; dextro- and lævo-α-benzylphenylallylmethylammonium salts." By W. J. Pope and A. W. Harvey.**

The authors have prepared in a state of purity a number of substances owing their optical activity to the presence of an asymmetric pentad nitrogen atom.

The externally compensated α-benzylphenylallylmethylammonium iodide of Wedekind when treated with silver *d*-camphorsulphonate yields *d*-benzylphenylallylmethylammonium *d*-camphorsulphonate, which melts at 171—173° and has the molecular rotation $[M]_D = +218{\cdot}1°$ in an aqueous solution containing one-fifth of a gram-molecule per litre; whence the value for the *d*-benzylphenylallylmethylammonium ion is $[M]_D = +166{\cdot}4°$. The residue from the preparation of this salt, when treated in aqueous solution with potassium iodide yields crude *l*-benzylphenylallylmethylammonium iodide which, on treatment with silver *l*-camphorsulphonate, gives the new salt, *l-benzylphenylallylmethylammonium l-camphorsulphonate*. This melts at 171—173° and has the molecular rotation $[M]_D = -210{\cdot}6°$ in an aqueous solution containing one-fourth of a gram-molecule per litre; the molecular rotation $[M]_D = -159{\cdot}0°$, is thence deduced for the ion of the *l*-base.

These salts when treated with potassium iodide in aqueous solution give crystalline precipitates of the corresponding iodides which may be crystallised from alcohol without undergoing inversion; they are soluble in cold chloroform, and in this solvent have the specific rotations $[\alpha]_D = +55{\cdot}2°$ and $[\alpha]_D = -53{\cdot}4°$ respectively. On warming the chloroform solutions, the rotation rapidly vanishes and a similar result is attained on allowing the cold chloroform solutions to stand for three days; the solutions on evaporation yield the externally compensated iodide in a state of purity, so that the inversion may be attributed to a dissociation into tertiary base and benzyl iodide.

The bromides are prepared in a similar manner and have the specific rotations $[\alpha]_D = +64{\cdot}1°$ and $[\alpha]_D = -65{\cdot}0°$ respectively in cold chloroform; the salts undergo inversion in chloroform just as the iodides do although appreciably less rapidly.

d-Benzylphenylallylmethylammonium nitrate,

$$C_7H_7{\cdot}N(C_6H_5)(C_3H_5)(CH_3)NO_3,$$

is a colourless crystalline substance melting at 164—165°, and in aqueous solution has the molecular rotation $[M]_D = +165{\cdot}3°$, a value

comparing well with that of the ion of the *d*-base deduced from the examination of the *d*-camphorsulphonate.

d-*Benzylphenylallylmethylammonium mercuri-iodide*,

$$C_7H_7\cdot N(C_6H_5)(C_3H_5)(CH_3)I,HgI_2,$$

is obtained as a bright yellow crystalline compound by heating the pure *d*-iodide with one equivalent of mercuric iodide in ethyl acetate solution; it melts at 125—127° and has the specific rotation $[\alpha]_D = +24{\cdot}4°$ in ethyl acetate solution. The enantiomorphously related salt also melts at 125—127°, and has the specific rotation $[\alpha]_D = -23{\cdot}0°$ in ethyl acetate. It is concluded that these mercuri-iodides contain quinquevalent nitrogen.

Attention was drawn to the persistency of the optical activity of these asymmetric nitrogen compounds except under the specific conditions which cause inversion. It should be noted that these substances are fundamentally distinguished from asymmetric carbon compounds in that they are electrolytes which, in aqueous solution, must be supposed to undergo electrolytic dissociation, giving an optically active ion of which the disrupted valency is one of those attached to the asymmetric atom; yet even under these conditions no inversion takes place.

Discussion.

Dr. Armstrong said that when Messrs. Pope and Peachey first stated that they had succeeded in obtaining optically active nitrogen compounds, he had pointed out that the discovery was of special importance, because it seemed at last to afford a means of deciding the long standing dispute as to the valency of nitrogen in the ammonium compounds. The discovery was not in itself sufficient to disprove the molecular hypothesis advocated by Kekulé, as it was possible to formulate the ammonium salts as molecular compounds, which it was conceivable might have a tetrahedral configuration. But the subsequent discovery of optically active sulphur compounds by Messrs. Pope and Peachey might be regarded as complete disproof of the molecular compound hypothesis, and it was consequently legitimate to argue that nitrogen acted as a pentad in the ammonium compounds. Nevertheless, there could be little doubt that the "superior" valency assumed by nitrogen in the ammonium compounds and by sulphur in the sulphonium compounds was in some way different in character from the lower or ordinary valency of these elements: that it was a "conditional" valency, as nitrogen became pentad and sulphur tetrad only under special conditions and in a very limited number of cases. There could be little doubt that the direction in which valency could act was of importance, and the inquiry into this must play an im-

portant part in the future. Reference was made to the behaviour of sulphur in thiophen as affording proof that the superior valency in some way became masked by the inclusion of the sulphur in the ring. The use made by the authors of the behaviour of double mercuric and platinic compounds as arguments against a change in valency was of a most ingenious character, as was also the reference to the evidence afforded by the stability of the active salts against the ionic dissociation hypothesis: the suggestion that a free affinity could not well act "materially" and serve to condition optical activity was particularly worthy of note.

Dr. HEWITT referred to Mr. Pope's remarks on the fact that the addition of mercuric iodide to optically active quaternary ammonium iodides gives rise to double salts in which the optical activity is preserved, and the conclusion drawn that the valency of nitrogen remains unchanged, and the extension of this argument to the valency of sulphur in the compounds of sulphonium iodides with metallic iodides. He considered it possible that the two active forms of a sulphonium iodide might add on mercuric iodide, the sulphur atom becoming hexavalent, and nevertheless the two resulting octahedral formulæ be related to one another as an object is to its image.

Dr. FORSTER suggested that the numerical difference between the rotation constants of *d*A*d*B and *l*A*l*B might disappear if *l*A*l*B were separated first, by adding *l*-camphorsulphonate to the racemic mixture, and inquired whether *l*-bromocamphorsulphonic acid would not be a useful substitute for *l*-camphorsulphonic acid. He questioned whether racemisation of the active ammonium iodide is due to dissociation on the lines indicated by Mr. Pope, pointing out that addition of ammonia should accelerate the change. Referring to the principle that a change of valency involves an alteration in the original valency directions, he wished to know why, if divalent sulphur forming part of a ring is prevented from becoming tetravalent on account of this principle, nitrogen does not lie under the same disability.

Dr. H. MCKENZIE asked whether Mr. Pope had had occasion to confirm Le Bel's resolution of inactive methylethylpropylisobutylammonium chloride by means of *Penicillium glaucum*; and, further, whether he had attempted to resolve Le Bel's substance by aid of an optically active acid, such as α-bromocamphorsulphonic acid.

Dr. MORGAN, in supporting the view that the nitrogen in the ring systems of the pyridine and acridine types is generally capable of assuming the quinquevalent condition, recalled the fact that naphthacridine readily combines with alkyl iodides yielding quaternary iodides so stable that they can be crystallised from hot aniline without decomposition, indicating thereby that the cyclic nitrogen is able to

maintain its quinquevalency, even in the presence of an amine containing a nitrogen atom free from constraint as regards the direction of its linkings.

Mr. W. J. Pope, in reply, observed that the new principle brought forward, namely, that during change of valency of an atom the valency directions might also change, appeared to be applicable when a bi- or quadri-valent sulphur atom became quadri- or sexa-valent respectively or when a quinquevalent nitrogen atom became septavalent; it is not necessarily applicable to the case of a tervalent nitrogen atom becoming quinquevalent because such a change might be effected by the two fresh groups attaching themselves to the nitrogen atom along a direction perpendicular to the plane containing the original three groups. The principle derived support from the fact that bivalent sulphur contained in a closed ring, and consequently restrained from altering its environment, cannot be caused to combine with alkyl iodides and become quadrivalent; the *n*-alkyl derivatives of piperidine and tetrahydroquinoline, on the other hand, combine with alkyl iodides at least as readily as do tertiary bases in which the nitrogen atom is not contained in a closed ring. *d*-Benzylphenylallylmethylammonium iodide undergoes inversion in chloroform solution about twice as rapidly as the corresponding bromide, but no experiments have yet been made with other salts. It is not immediately apparent how the inversion of optically active stannomethyl derivatives can be caused by dissociation, but the inversion is possibly due to dissociation of the stannic compound into a stannous compound and an alkyl salt.

***80. "Reactions of hydroxyoxamides." By R. H. Pickard and W. Carter.**

Hydroxyoxamide and its mono-phenyl-, *p*-tolyl-, *α*- and *β*-naphthyl-derivatives, $RNH{\cdot}CO{\cdot}CONHOH$, react as hydroxamic acids. The general reactions of hydroxamic acids (Thiele and Pickard, *Ann.*, 1899, **309**, 189) can be carried out with these compounds, giving quantitative yields of substituted biurets, carbonyl di-carbamides, and allophanates.

The monosubstituted phenyl-, *p*-tolyl-, *α*- and *β*-naphthyl-biurets, analogously substituted ethyl allophanates, and the *sym*-disubstituted carbonyl di-carbamides, $CO(NHCONHR)_2$, were described.

The acetate of oxalodihydroxamic acid described by Hantzsch (*Ber.*, 1894, **27**, 801), is apparently a diacetate; it is acid in properties, and dissolves in a solution of sodium carbonate, giving a solution which, after warming, contains small quantities of hydrazine.

***81. "The *sym*-trichlorobromoanilines; and chloro- and bromo-amino-derivatives of chlorobromoacetanilides." By F. D. Chattaway and K. J. P. Orton.**

The authors called attention to the great resemblance existing between the two similarly constituted *sym*-chlorodibromoanilines and their acetyl derivatives respectively. There is a similar resemblance between the two *sym*-dichlorobromoanilines. The acetylchloroamino-derivatives, however, serve to distinguish the one isomeric aniline from the other, as they possess melting points lying several degrees apart.

The following compounds have been prepared: 4-*chloro*-2 : 6-*dibromoaniline*, $C_6H_2ClBr_2 \cdot NH_2$ (first prepared by Hofmann, *Ann.*, 1845, **53**, 38), needles, melting at 97° (Hofmann does not record the melting point) and boiling at 301° under 760 mm. pressure; 4-*chloro*-2 : 6-*dibromoacetanilide*, $C_6H_2ClBr_2 \cdot NHAc$, flattened prisms or needles, melting at 226—227°; *acetylchloroamino*-4-*chloro*-2 : 6-*dibromobenzene*, $C_6H_2ClBr_2 \cdot NClAc$, short, four-sided prisms melting at 110—111°; 2-*chloro*-4 : 6-*dibromoaniline*, $C_6H_2ClBr_2 \cdot NH_2$ (first prepared by Langer, *Ann.*, 1882, **215**, 115), needles, closely resembling the isomeric aniline and melting at 95°; 2-*chloro*-4 : 6-*dibromoacetanilide*, $C_6H_2ClBr_2 \cdot NHAc$, flattened prisms or needles, melting at 227°; *acetylchloroamino*-2-*chloro*-4 : 6-*dibromobenzene*, $C_6H_2ClBr_2 \cdot NClAc$, four-sided prisms, melting at 99—100°; 2 : 6-*dichloro*-4-*bromoaniline*, $C_6H_2Cl_2Br \cdot NH_2$ (first prepared by Fittig and Büchner, *Ann.*, 1877, **188**, 22), needles, melting at 92° (Fittig and Büchner give 93·5°); 2 : 6-*dichloro*-4-*bromoacetanilide*, $C_6H_2Cl_2Br \cdot NHAc$, flattened prisms or needles melting at 214°; *acetyl chloroamino*-2 : 6-*dichloro*-4-*bromobenzene*, $C_6H_2Cl_2Br \cdot NClAc$, prisms melting at 81°; 2 : 4-*dichloro*-6-*bromoaniline*, $C_6H_2Cl_2Br \cdot NH_2$, needles melting at 83·5°; 2 : 4-*dichloro*-6-*bromoacetanilide*, $C_6H_2Cl_2Br \cdot NHAc$, flattened prisms or needles melting at 218°; *acetylchloroamino*-2 : 4-*dichloro*-6-*bromobenzene*, $C_6H_2Cl_2Br \cdot NClAc$, four-sided prisms melting at 91—92°; 2 : 6-*dibromoacetanilide*, $C_6H_3Br_2 \cdot NHAc$, prisms melting at 208—209°; *acetylchloroamino*-2 : 6-*dibromobenzene*, $C_6H_3Br_2 \cdot NClAc$, short prisms melting at 88°; *acetylbromoamino*-4-*chlorobenzene*, $C_6H_4Cl \cdot NBrAc$, yellow plates melting at 91°; *acetylchloroamino*-4-*bromobenzene*, $C_6H_4Br \cdot NClAc$, rhombs melting at 108—109°; *acetylbromoamino*-2 : 4-*dichlorobenzene*, $C_6H_3Cl_2 \cdot NBrAc$, yellow plates or prisms melting at 95—96°; *acetylchloroamino*-4-*chloro*-2-*bromobenzene*, $C_6H_3ClBr \cdot NClAc$, four-sided prisms melting at 74—75°; *acetylbromoamino*-4-*chloro*-2-*bromobenzene*, $C_6H_3ClBr \cdot NBrAc$, yellow rhombs melting at 85—86°; *acetylchloroamino*-2-*chloro*-4-*bromobenzene*, $C_6H_3ClBr \cdot NClAc$, rhombs or prisms melting at 88—89°; *acetylbromoamino*-2-*chloro*-4-*bromobenzene*,

$C_6H_3ClBr{\cdot}NBrAc$, yellow, four-sided prisms melting at 110—111°; *acetylchloroamino*-2 : 4-*dibromobenzene*, $C_6H_3Br_2{\cdot}NClAc$, plates or rhombs melting at 56—57°; *acetylchloroamino*-2 : 4 : 6-*tribromobenzene*, $C_6H_2Br_3{\cdot}NClAc$, prisms melting at 109—110°.

***82. "Replacement of bromine by chlorine in anilines." By F. D. Chattaway and K. J. P. Orton.**

When tribromoaniline ($NH_2 : Br : Br : Br = 1 : 2 : 4 : 6$) reacts with acetylchloroamino-2 : 4-dichloroacetanilide in chloroform solution, bromine is evolved, and in addition to an azo-derivative and another coloured substance, a chlorodibromoaniline can be isolated. This aniline proves to be 4-chloro-2 : 6-dibromoaniline. With *sym*-chlorobromoanilines (2-chloro-4 : 6-dibromoaniline, 4-chloro-2 : 6-dibromoanilines, 2 : 4-dichloro-6-bromoaniline, and 2 : 6-dichloro-4-bromoaniline), it was observed that bromine was given off to a far greater extent from those anilines which possessed a bromine atom in the para-position relatively to the amino-group. Again, an aniline in which bromine had been replaced by chlorine could only be isolated in the case of those anilines where bromine originally occupied the para-position. Thus, 2 : 4-dichloro-6-bromoaniline could be obtained from 2-chloro-4 : 6-dibromoaniline, but not from 4-chloro-2 : 6-dibromoaniline.

Acetylchloroamino-2 : 4 : 6-tribromobenzene (and similar derivatives of chlorobromobenzenes) gives off bromine when heated in a sealed tube with acetic acid. No pure chlorobromoacetanilide has been isolated.

***83. "The absorption spectra of cyanogen compounds." By W. N. Hartley, F.R.S., J. J. Dobbie, D.Sc., M.A., and A. Lauder, B.Sc.**

The authors described the results of an examination of the absorption spectra of cyanogen compounds, more particularly of cyanuric acid, melamine and their respective esters.

Cyanuric acid and methyl cyanurate (m. p. 135°) are commonly represented as closed chain compounds in which the chain is formed of alternate atoms of carbon and nitrogen alternately doubly and singly linked, while methyl *iso*cyanurate (m. p. 175°) is represented as a derivative of *iso*cyanuric acid containing three keto-groups and having the carbon and nitrogen atoms only singly linked. From the circumstance that pyridine, dimethylpyrazine and other similar substances, in which the carbon and nitrogen atoms are united by alternate double and single linkings, exhibit strong absorption bands, it was expected that cyanuric acid and its esters would likewise exhibit marked selective

absorption. On the other hand, it was anticipated that the esters of *iso*cyanuric acid would behave like piperidine and other substances composed of a closed chain of singly linked carbon and nitrogen atoms. The authors found, however, no trace of selective absorption in any of the substances examined, and pointed out that in the absence of more satisfactory chemical evidence it is questionable whether the constitution of cyanuric acid ought to be represented by a structural formula so closely analogous to that of pyridine and of dimethylpyrazine.

The spectrographic examination confirms the view generally accepted on the evidence of chemical reactions, that cyanuric acid and methyl cyanurate (m. p. 135°) are similarly constituted and that the relations between melamine and triethylmelamine (m. p. 74°) are correctly represented by the commonly accepted formulæ.

84. "The nutrition of yeast. Part III." By A. L. Stern, D.Sc.

The author has determined the effect of varying the concentration of the sugar, the temperature of fermentation, the amount of seed-yeast, and the time, on the nutrition of yeast.

The experiments were made in exactly the same manner as those previously described (*Trans.*, 1899, **75**, 202); the sugar used was dextrose, the nitrogenous nutriment, asparagine; and the inorganic nutriment, potassium phoshate, magnesium sulphate and calcium sulphate; and the yeast a pure culture from a Burton pitching yeast.

The conclusions drawn are:—

(1) Any increase of nitrogenous or inorganic nutriment beyond a definite limit will not increase either the amount of nitrogen assimilated by the yeast, or the weight of the yeast. This limit is but little greater than the largest amount which the yeast is able to assimilate under the conditions of the experiment.

(2) Any increase of the sugar is accompanied by an increase of the weight of nitrogen assimilated and of the weight of the yeast. This increase goes on up to the strongest concentrations which can be completely fermented. The rate of increase is greatest at the lowest concentrations, and falls off gradually as the concentration rises.

(3) Temperatures between 12° and 25° have but little influence on the weight of nitrogen assimilated and the weight of the yeast crop. At higher temperatures reproduction is weakened.

(4) The weight of the nitrogen assimilated and of the yeast crop is composed of two quantities: the weight of the seeding *plus* a quantity dependent on the composition of the solution.

(5) The growth of the yeast is during a portion of the fermentation

proportional to the amount of sugar fermented, and proceeds as long as any sugar remains unfermented.

From a consideration of these deductions, and of the work of others, the author concludes that there is an essential difference between the functions of the inorganic and nitrogenous nutriment on the one hand, and of the sugar on the other; that the former supply only material to the yeast, whilst the latter supplies both material and energy. Whether fermentation is caused by an enzyme or not, the author does not yet consider definitely determined, whilst there is certain amount of evidence to support this supposition, there is none to negative it.

85. "On the colloid form of piperine, with especial reference to its optical refraction and dispersion." By H. G. Madan.

The author has examined the conditions under which crystalloid piperine is converted into the colloidal allotropic form of the substance. He finds that while crystallised piperine when heated to its melting point, 135°, solidifies on cooling into a transparent resin-like substance, the latter, when thus prepared, is not permanent, but reverts spontaneously in the course of a few months into the crystalloid form. The same change takes place quickly and completely when the substance is heated to 100°. If, however, piperine is kept for an hour at a temperature of 180°, the resulting product is much more stable if not absolutely permanent as a colloid. It does not become crystalline when heated to 100° or above, nor has the lapse of $2\frac{1}{2}$ years had any effect in changing it back into the crystalloid condition.

The results of a determination of the refractive indices of colloid piperine for some of the principal spectrum lines were given, from which it appears that, while its refraction is very high ($\mu_D = 1{\cdot}684$), its dispersion is quite extraordinary, the visual spectrum being nearly four times as long as that given by a prism of dense flint glass having the same refracting angle. The coefficient of dispersion ($\mu_{H_\gamma} - \mu_{H_\alpha}$) is 0·142, while that of carbon disulphide is only 0·057.

86. "Note on pyromucylhydroxamic acid." By R. H. Pickard and A. Neville.

The reactions of pyromucylhydroxamic acid have been studied with a view to obtaining the furan carbamides and carbamates by the method of Thiele and Pickard. These are, however, uncrystallisable oils, which decompose on hydrolysis. *Pyromucylhydroxamic acid*, $C_4H_3O{\cdot}CONHOH$, obtained by hydrolysing ethyl pyromucate with hydroxylamine, melts at 124° and forms a *benzoyl* derivative, which melts at 134°.

87. "The condensation of ethylphenylketone with benzaldehyde." By R. D. Abell, B.Sc.

Under the influence of a 20 per cent. solution of sodium ethylate, ethylphenylketone reacts with benzaldehyde to form (1) 1 : 3-diphenyl-2-methyl-trimethylene glycol, colourless needles m. p. 98—99°; (2) impure benzalpropiophenone, as a yellow oil, boiling at 210—213° (23 mm.); (3) 1 : 3-dimethyl-1 : 3-dibenzoyl-2-phenylpropane, $C_{25}H_{24}O_2$, plates, m. p. 162—163°.

If sodium methylate be similarly employed, only the first two are obtained, whilst a solution of potassium hydroxide in aqueous alcohol gives only benzalpropiophenone, which may be more satisfactorily prepared by using hydrochloric acid gas as the condensing agent.

If the first substance (the glycol) be oxidised by means of chromic acid, methyldibenzoylmethane is produced, and this, by the action of hydrazine hydrate, gives 3 : 5-*diphenyl*-4-*methylpyrazole* which melts at 222—223°.

Benzalpropiophenone readily unites with bromine to form *benzalpropiophenone dibromide*, which is obtained as a viscid green oil by adding a solution of bromine in chloroform to one of benzalpropiophenone in the same solvent. Benzalpropiophenone with phenylhydrazine gives a *hydrazone*, $C_{22}H_{20}N_2$, yellow needles, m. p. 127—128°.

As it seemed probable that for the preparation of the third substance the previous formation of benzalpropiophenone was necessary, a mixture of equimolecular quantities of benzalpropiophenone and ethylphenylketone was treated with sodium ethylate, when a compact crystalline mass was obtained which by recrystallisation from alcohol was separated into two isomeric compounds having the formula $C_{25}H_{24}O_2$, one in the form of plates, m. p. 162—163°, identical with the 1 : 3-dimethyl-1 : 3-dibenzoyl-2-phenylpropane mentioned above, and the other as needles, m. p. 121—122°.

Sodium methylate cannot be used instead of the ethylate in this reaction.

When the isomeride, m. p. 162—163°, was heated with alcoholic ammonia, much resinous matter was formed together with a small quantity of a substance crystallising in needles, m. p. 155—156°, which from the percentage of nitrogen found may be either triphenyldimethyl dihydropyridine, $C_{25}H_{23}N$, or triphenyldimethyl pyridine, $C_{25}H_{21}N$.

This substance was also obtained by the action of hydroxylamine hydrochloride on both isomerides.

88. "A new method for the determination of hydrolytic dissociation." By R. C. Farmer, B.Sc., Ph.D.

The usual method for the determination of hydrolytic dissociation by the velocity of saponification of an ester is not applicable in certain cases, particularly those in which the acid or base under investigation is difficultly soluble in water and is precipitated during the reaction. The author has therefore devised a new method, in which the free acid or base is determined by distribution between two solvents.

An aqueous solution of the salt of a weak acid or base is shaken with a known amount of benzene or some other suitable solvent, which extracts only one of the dissociation products. From the amount extracted, the degree of hydrolysis of the salt can be calculated, the coefficient of distribution for the substance between the two solvents having been previously determined. The method was tested with a salt of hydroxyazobenzene. The values obtained at different dilutions agreed with those required by the law of dilution given by Arrhenius. The mean values found for the hydrolytic dissociation of a salt of hydroxyazobenzene at 25° were as follows:

Dilution in litres	32	50	64	80	100
Percentage hydrolysis.....	0·91	1·09	1·24	1·32	1·60

Owing to the intense colour of the hydroxyazobenzene, the estimations had to be carried out gravimetrically. In most cases, volumetric methods could be used with advantage, both as regards rapidity and accuracy. Similar experiments with weak bases have not yet been attempted.

89. "The production of some new metallic borides." By S. A. Tucker, Ph.B., and H. R. Moody, B.S., M.A.

The authors describe the formation and properties of four new borides, those of zirconium, chromium, tungsten and molybdenum. These compounds were prepared by bringing an intimate mixture of the metal with boron under the influence of a temperature produced by a current of from 200 to 275 amperes and 60 to 75 volts in the electric furnace.

Combination takes place in a few minutes with the formation of compounds which are crystalline, hard, of a high specific gravity, not easily attacked by acids, and having very high melting points. The compounds thus prepared have the following formulæ Zr_3B_4, CrB, WB_2, and Mo_3B_4.

The authors were unable to produce the borides of copper and of

bismuth in a like manner, and it seems therefore as if boron had no affinity for the members of the copper group, but that it combines readily with the members of the iron group.

90. "The action of lead thiocyanate on the chlorocarbonates. Part II. Carboxymethyl- and carboxyamyl-thiocarbimides and their derivatives." By R. E. Doran.

The author has already described (*Trans.*, 1896, **69**, 324) the preparation and properties of carboxyethylthiocarbimide and its derivatives, and this continuation of his work deals chiefly with the thiocarbamides, thioureas, and thiocarbamates obtained from its methyl and amyl homologues. No attempt was made in this case to isolate the parent substances, but the following compounds were prepared, identified, and are described in detail.

ab-*Carboxymethylphenylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$, white needles, m. p. 158°; ab-*carboxymethylbenzylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$, needles, m. p. 134°; ab-*carboxymethyl-o-tolylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$, needles, m. p. 172°; ab-*carboxymethyl-p-tolylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$, short prisms, m. p. 158°; ab-*carboxymethyl-α-naphthylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$, needles, m. p. 193°; ab-*carboxymethyl-β-naphthylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$, minute needles, m. p. 184°; ab-*carboxymethylmethylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_3$, needles, m. p. 146°; ab-*carboxymethylethylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_2H_5$, needles, m. p. 86°; ab-*carboxymethylisobutylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_4H_9$, long prisms, m. p. 83°; *carboxymethylthiourea*, $CH_3O{\cdot}CO{\cdot}N{:}C(NH_2)SH$, short prisms, m. p. 166°; *carboxymethylpiperidylthiourea*, $CH_3O{\cdot}CO{\cdot}N{:}C(SH){\cdot}N{:}C_5H_{10}$, needles, m. p. 97°; *carboxymethylphenylsemithiocarbazide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}C(SH){:}N{\cdot}NH{\cdot}C_6H_5$, glistening plates, m. p. 180°; *methyl carboxymethylthiocarbamate*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OCH_3$, feathery needles, m. p. 46°; *ethyl carboxymethylthiocarbamate*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OC_2H_5$, needles, m. p. 83°; *benzyl carboxymethylthiocarbamate*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OCH_2{\cdot}C_6H_5$, cream-white needles, m. p. 103°.

Derivatives of carboxyamylthiocarbamide:

ab-*Carboxyamylphenylthiocarbamide*, $C_5H_{11}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$, white needles, m. p. 97—98°; ab-*carboxyamyl-o-tolylthiocarbamide*, $C_5H_{11}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$, white needles, m. p. 96—97°.

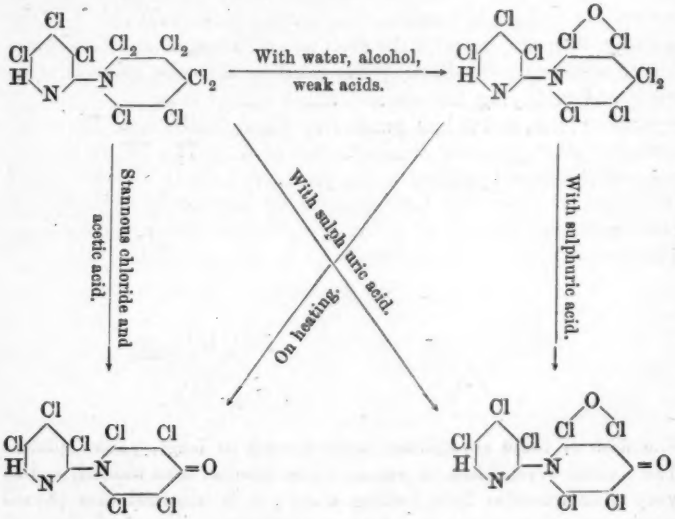
Carboxyamylthiourea was also obtained, but in too small a quantity to permit of its satisfactory identification.

91. "The chlorine derivatives of pyridine. Part VII. Some condensation products." By W. J. Sell, M.A., F.R.S., and F. W. Dootson, M.A.

A series of experiments having for their object the determination of the orientation of a compound, $C_{10}HCl_{11}N_2$, which has been obtained by the action of chlorine on pyridine hydrochloride, together with certain of its derivatives (*Trans.*, 1899, **75**, 980) was described.

This substance, which is the principal product of the chlorination, may be crystallised unaltered from chloroform or acetone, but if the solvent contains the hydroxyl group the compound is decomposed. With benzoic and other acids it reacts, giving a theoretical yield of the acid chloride in accordance with the equation $C_{10}HCl_{11}N_2 + C_6H_5CO_2H = C_6H_5COCl + C_{10}HCl_9N_2O + HCl$.

The following formulæ exhibit the relationship between the parent compound and certain of its derivatives :

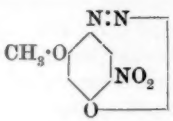


92. "The diazotisation of dinitroanisidine and the constitution of the resulting product." By R. Meldola, F.R.S., and J. V. Eyre.

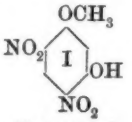
A PAPER just published by Freyss (*Bull. Soc. Ind. de Mulhouse*, 1901, **70**, 375) anticipates some conclusions at which the authors have arrived as the outcome of an investigation upon which they have been engaged since last October. They are led, therefore, to place upon

record the results of those experiments which appear to give independent support to the conclusions of the author above named. This work is an extension of that already published (Meldola and Wechsler, *Trans.*, 1900, **77**, 1172; *Proc.*, 1898, **14**, 226).

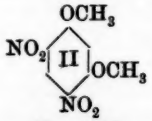
The crystalline diazo-compound, obtained by the action of a nitrite on dinitroanisidine in acetic acid solution, is a diazoxide of the formula:



The proof of this constitution is given by several considerations, some of which appear from the experiments of Freyss, the most cogent, perhaps, being its ready convertibility into nitromethylresorcinol, $C_6H_3 \cdot NO_2 \cdot OH \cdot OCH_3 = 1:2:4$. The authors find the most convenient method for bringing about this conversion is to dissolve the diazoxide in alcoholic sodium hydroxide. The decomposition takes place at the ordinary temperature, with the evolution of nitrogen and the formation of aldehyde. On diluting the alkaline alcoholic solution with water and acidifying, the nitroresorcinol methyl ether separates in a crystalline form, and is best purified by steam distillation. The nitroresorcinol ether gives the dimethyl ether of m. p. 72—73° on methylation with dimethyl sulphate in the presence of alkali. The mono- and the di-methyl ethers are both nitrated by solution in cold, fuming nitric acid, the dimethyl ether dissolving at first with a green colour. The corresponding dinitro-derivatives have the constitutions:



M. p. 110·5°.



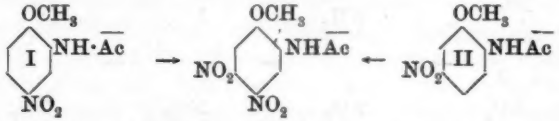
M. p. 154°.

The first of these crystallises from alcohol in large, yellow plates. The second crystallises in small, white needles from alcohol, and in very minute needles from boiling water; it is obtained also (mixed with colouring matters) by the direct nitration of resorcinol dimethyl ether in acetic acid with excess of fuming nitric acid, and its constitution as a derivative of resorcinol is thus confirmed. The nitroresorcinol monomethyl ether benzoylates very readily by the Schotten-Baumann method. The benzoyl derivative, $C_6H_3 \cdot NO_2 \cdot OC_7H_5O \cdot OCH_3 = 1:2:4$, crystallises from alcohol in flat, white needles melting at 95°. The nitro-derivative, when dissolved in acetic acid, gives an intense blue colour on the addition of zinc dust. If reduced with zinc dust and

acetic acid in the presence of acetic anhydride, the acetamino-derivative, $C_6H_3 \cdot NHAc \cdot OH \cdot OCH_3 = 1:2:4$, is obtained. This crystallises from water in lustrous, flat, white needles, which become brown on exposure to the air. The melting point is 164—165°.

The diazoxide is remarkably stable towards acids; it can be boiled with dilute hydrochloric or sulphuric acid and can be crystallised from boiling glacial acetic acid or from acetic anhydride without undergoing decomposition. It is decomposed on boiling with hydriodic acid solution and the product is iodonitroresorcinol methyl ether (Meldola and Wechsler, *loc. cit.*, 1173), $C_6H_2 \cdot OCH_3 \cdot OH \cdot NO_2 \cdot I = 1:3:4:6$. The azo-$\beta$-naphthol derivative described in the former note (*loc. cit.*) has the formula $C_6H_4 \cdot NO_2 \cdot OCH_3 \cdot OH \cdot N_2 \cdot C_{10}H_6 \cdot OH$. In addition to the properties already assigned to this compound, it may be added that it is distinctly phenolic in character, dissolving in cold aqueous alkali with a dull claret-red colour and being precipitated unchanged by acids. The phenolic character is due to the hydroxyl group in the para-position. An examination of the product of the action of ammonium sulphide on the azo-compound has shown that no amino-azo-compound is formed, and this is in accordance with the view that the nitro-group is not in the para-position with respect to the azo-group (Meldola, *Trans.*, 1883, **43**, 425).

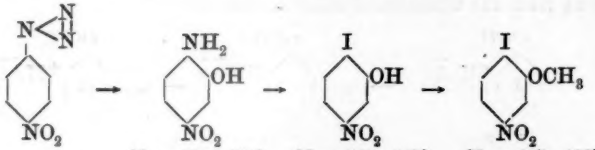
The constitution of dinitroanisidine (m. p. 188°) first described (Meldola and Wechsler, *loc. cit.*) follows from the fact that it is obtainable by the further nitration of *both* the nitroacetanisidides resulting from the nitration of *o*-acetanisidide:



The authors have proved this directly by the nitration of carefully purified specimens of the mononitroacetyl derivatives. No. I was prepared by the reduction of dinitroanisole and acetylation of the nitroanisidine (Meldola, Woolcott, and Wray, *Trans.*, 1896, **69**, 1330). No. II was prepared from the corresponding nitroanisidine, the latter being obtained pure, by a modification of the method formerly described (*Proc.*, 1898, **14**, 226). The mixture of nitroacetyl derivatives resulting from the nitration of *o*-acetanisidide is boiled with dilute alkali till completely hydrolysed. The mixed nitroanisidines on being dissolved in hot dilute sulphuric acid deposit, on cooling, silvery scales of the sulphate of the *p*-nitro-compound, $C_6H_3 \cdot NO_2 \cdot NH_2 \cdot OCH_3 = 1:4:5$, the sulphate of the isomeric compound remaining in solution. The crystalline sulphate gives pure *p*-nitro-*o*-anisidine on treatment with dilute alkali and crystallisation of the product from hot

water. In order to characterise further the two nitroanisidines and the dinitroanisidine, the benzoyl derivatives have been prepared: $C_6H_3 \cdot NO_2 \cdot NH(C_7H_5O) \cdot OCH_3 = 1:4:5$, white silky needles from alcohol, m. p. 149—150°; $C_6H_3 \cdot NO_2 \cdot NH(C_7H_5O) \cdot OCH_3 = 1:3:4$, slender ochreous neeedles from alcohol, m. p. 160—161°; $C_6H_2 \cdot (NO_2)_2 \cdot NH(C_7H_5O) \cdot OCH_3 = 1:2:5:4$, ochreous scales from acetic acid, m. p. 185—186°.

The constitution of the *p*-nitro-*o*-anisidine was proved by two methods differing from those adopted by Freyss, as well as by conversion into the *p*-nitro-guaiacol of m. p. 104°. The latter compound, of which the discovery is assigned to Rupe (*Ber.*, 1897, **30**, 2446), was first described by one of the authors (Meldola, *Proc.*, 1896, **12**, p. 125). The *p*-nitro-*o*-anisidine when diazotised and the amino-group replaced by iodine in the usual way, gave an iodonitroanisole which crystallised in straw-coloured needles melting at 127°—128°. The constitution of this compound might have been expected to correspond with that of the nitro-aminophenol, m. p. 201°—202°, obtained by Friedländer and Zeitlin (*Ber.*, 1894, **27**, 196) by heating *p*-nitrobenzenediazimide with sulphuric acid. Some of the nitroaminophenol was prepared by this method and converted into the corresponding iodonitrophenol which crystallises from alcohol in ochreous needles melting at 146°—147°. The silver salt of the latter, which is a brick-red amorphous powder, on treatment with methyl iodide, gave the same iodonitroanisole m. p. 127°—128°, as that obtained from *p*-nitro-*o*-anisidine:



M. p. 201—202°. M. p. 146—147°. M. p. 127—128°.

The other method consisted in combining the diazotised nitroanisidine with β-naphthol in the usual way and reducing the nitroazo-compound to an aminoazo-compound by ammonium sulphide. The nitroazo-compound is obtained as a scarlet precipitate on mixing solutions of the diazonium salt and β-naphthol dissolved in sodium hydroxide. It crystallises from glacial acetic acid, in which it dissolves with difficulty, in filamentous needles of a dull red colour with a slight metallic reflex. Its melting point is 269°. It dissolves in alcoholic soda with a violet colour and with a similar colour in strong sulphuric acid, the latter solution becoming redder on dilution with water. The solution in alcoholic soda becomes red on heating with ammonium sulphide and on dilution with water the aminoazo-compound, $NH_2 \cdot C_6H_3 \cdot OCH_3 \cdot N_2 \cdot C_{10}H_6 \cdot OH$, separates out in bronzy scales. The

melting point of this compound is above 300°. It dissolves in alcohol with a bordeaux-red colour which becomes orange on adding hydrochloric acid. It dissolves in hot aqueous hydrochloric acid with a dull red and in strong sulphuric acid with a magenta-red colour, becoming more orange on dilution. The reducibility of the nitro-group without the separation of the nitrogen atoms of the azo-group may be taken as proof that the two groups are in the para-position with respect to one another.

The constitution of the nitroanisidine of Cahours (Meldola, Woolcott, and Wray, *loc. cit.*) was further proved by converting it into the corresponding iodonitroanisole by replacing the amino-group by iodine by the diazo-method. The iodonitroanisole, $C_6H_3 \cdot NO_2 \cdot I \cdot OCH_3$ = 1 : 3 : 4, melts at 95—96° and is identical with that described by Reverdin (*Ber.*, 1896, **29**, 998).

Experiments were in progress to obtain direct evidence of the constitution of the dinitroanisidine at the time of appearance of the paper by Freyss. The triaminoanisole obtained by reducing the dinitroanisidine with tin and hydrochloric acid forms a crystalline hydrochloride, but it is very unstable, passing readily into a deep violet colouring matter on exposure to the air. The dinitroacetanisidide does not give an anhydro-base on reduction, an observation which is in harmony with the view that the acetamino-group is not in the ortho-position with respect to a nitro-group. On the other hand, that the triaminoanisole contains two amino-groups in the ortho-position is proved by the formation of an azine with phenanthrenequinone. On heating together equimolecular weights of the triamine and the quinone in glacial acetic acid, the aminoazine is gradually formed, and on adding hydrochloric acid the hydrochloride is completely thrown out on cooling as a dull red precipitate. The free base is an ochreous powder which dissolves in alcohol with a magnificent green fluorescence. It does not readily crystallise, but separates from boiling toluene in the form of brown nodules having a melting point of about 237°, but softening before this temperature. The base thus obtained contains one molecule of toluene and has the formulæ :

$$CH_3O \cdot NH_2 \cdot C_6H_2 \begin{cases} N \cdot C \cdot C_6H_4 \\ N \cdot C \cdot C_6H_4 \end{cases} + C_7H_8.$$

The result of this investigation thus confirms the conclusion that on diazotising 3 : 4-dinitro-*o*-anisidine in acetic acid, it is the 4-nitro-group which is eliminated, probably in accordance with the scheme :

$$CH_3O \cdot NO_2 \cdot C_6H_2 \begin{cases} N_2 \cdot O \cdot H \\ NO_2 \end{cases} = CH_3O \cdot NO_2 \cdot C_6H_2 \begin{cases} N_2 \\ O \end{cases} + HNO_2.$$

The more exact nature of the mechanism of the change will be made the subject of further investigation.

ADDITIONS TO THE LIBRARY.

I. Donations.

Cohen, J. B. Practical organic chemistry for advanced students. London 1900. From the Author.

II. By Purchase.

Ahrens, F. B. Anleitung zur chemisch-technischen Analyse. Ill. Stuttgart 1901.

Meyer, O. E. The kinetic theory of gases: elementary treatise, with mathematical appendices. Translated from the second revised edition by R. E. Baynes. London 1899.

Bredig, Georg. Anorganische Fermente. Ill. Leipzig 1901.

Klöcker, A. Die Gärungsorganismen in der Theorie und Praxis der Alkoholgärungsgewerbe. Ill. Stuttgart 1900.

Migula, W. Compendium der bakteriologischen Wasseruntersuchung nebst vollständiger Uebersicht der Trinkwasserbakterien. Ill. Wiesbaden 1901.

Nietzki, Rudolf. Chemie der organischen Farbstoffe. Fourth edition. Berlin 1901.

Wedekind, Edgar. Die heterocyklischen Verbindungen der organischen Chemie. Leipzig 1901.

Pamphlets.

Wendt, Gustav. Ueber einige unvollkommenheiten des Substanzgesetzes und ihre Abstellung. Berlin 1900.

Wislicenus, Johannes. Sir Edward Frankland. Leipzig 1901. From the Author.

At the next meeting, on Thursday, June 6th, the following papers will be communicated:—

"A laboratory method for the preparation of ethylene." By G. S. Newth.

"Oroxylin." By W. A. H. Naylor and C. S. Dyer.

"Some relations between physical constants and constitution in benzenoid amines. II." By P. Gordon and L. Limpach.

"The constitution of the acids obtained from α-dibromocamphor." By A. Lapworth and W. H. Lenton.

"The decomposition of chlorates. IV. The supposed mechanical facilitation of the decomposition of potassium chlorate." By W. H. Sodeau.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before June 10th.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, June 20th, 1901.

Adams, Ormsby Gore,
Stawell, Victoria, Australia.

Lecturer on Chemistry and Mineralogy, &c. Studied Chemistry, &c., at Otago University (New Zealand University) for three years, 1896—1898. Was Assayer and Analyst at Tasmanian Smelting Company's Works at Zeehan, Tasmania, 1900. At present, Lecturer on Chemistry, Mineralogy, &c., at Stawell School of Mines, Victoria, Australia. Holds Diploma of Associate of Otago University School of Mines, and also Certificate of Metallurgical Chemist and Assayer from the same institution.

Orme Masson. — Fred. W. Steel.
D. Avery. — *C. R. Blackett.*
A. W. Craig.

Ashwell, Guy,
Standard Bank, Bulawayo.
Analytical Chemist and Assayer.

Charles M. Stuart. — Thomas Purdie.
Frank Clowes. — *J. Emerson Reynolds.*
Edward T. Shelbourn.

Aspinall, Thomas,
42, Gilnow Road, Bolton.

Analytical Chemist. Research in Sewage Purification and general interest in Chemistry.

Walter Ratcliffe, — William B. Mason.
Jno. L. Whiteside. — *Frank Scudders.*
J. Carter Bell. — *George J. Allen.*

Aston, William George,

4, Dalkeith Road, Ilford.

Chemist in the Laboratory of the Gas Light and Coke Company's Tar Product Works, Beckton. Scholar for three years at People's Palace Day Schools. Scholar for two years at the East London Technical College (People's Palace) Day Classes. Passes in Honours at the South Kensington Examinations in Organic Chemistry, Theoretical and Practical, and Inorganic, Practical. Joint Author with Dr. Hewitt of papers, "Bromination of Benzeneazophenol" (*Trans.*, 1900, 77, 712); "Bromination of Benzeneazophenol," Part II (*Trans.*, 1900, 77, 810).

J. T. Hewitt.	Edgar S. Barralet.
Frank Dixon.	William A. Rugginz.
T. Wilton.	Samuel Clift.

Barker, Hubert Haigh,

3, Waverley Place, St. John's Wood, N.W.

Analytical Chemist. Articled pupil to Professor Bayne for three years in Analytical Chemistry; at present, junior Assistant and Demonstrator at the Royal Veterinary College.

James Bayne.	W. B. Bottomley.
Hubert E. Lindley.	*Percy A. E. Richards.*

Bernard Dyer.

Beaven, Edwin Sloper,

5, Boreham Terrace, Warminster.

Maltster and Chemist. Interested in the Chemistry of Agriculture and Malting. Author, with J. M. H. Munro, D.Sc., of papers in *J. R. Agricultural Society*, on "Manurial Conditions Affecting the Quality of Malting Barley," March, 1897, and June, 1900.

J. Henry Gilbert.	N. Story Maskelyne.
Samuel Rideal.	E. R. Moritz.
John M. H. Munro.	Horace T. Brown.

Bedford, Fred,

9, Market Place, Sleaford, Lincs.

Teacher of Chemistry. Three years' practical experience in the Analysis of Water and Food-stuffs, and in Organic Chemistry generally. Second Class Honours in Chemistry at London Inter. B.Sc. Advanced Stage Certificates Science and Art Department, Inorganic and

Organic Chemistry. Lecturer in Chemistry under Kesteven County Council. Desirous of increasing my knowledge of Chemistry.

Reginald B. Brown.	*J. T. Hewitt.*
Hudson Donaldson.	*Chapman Jones.*
Alex. W. Bain.	*James C. Philip.*
J. H. Allworthy.	*John McCrae.*

Bridges, Joseph Samuel,

45, Thistlewaite Road, Clapton, N.E.

Principal, Walthamstow Science and Technical Institute, Senior Professor of Biology, City of London College. B.Sc. Lond.; Honours in Chemistry. Lecturer and Demonstrator in London laboratories for 17½ years. Research in Physiological Chemistry at King's College.

Isaac Sydney Scarf.	E. J. Jackman.
Chapman Jones.	Harold W. Harrie.

J. C. Mascarenhas.

Crabtree, Arthur,

9, Bigg Market, Newcastle-on-Tyne.

Science Lecturer in Physiology, Hygiene and Chemistry. Science Lecturer in Newcastle Day and Evening Schools. Student of Chemistry, Elem., Adv., and Honours, for six years under Drs. C. Gerland, R. H. Pickard, and G. Smith, and obtained many certificates. For a few years Teacher of Physiology and Hygiene under the Science and Art Depart. The Society's publications would be most useful to me in my further studies and labours.

Robert H. Pickard.	Wm. Lewins.
T. W. Lockwood.	C. Gerland.
R. S. Cahill.	*James Foulds.*

Dean, George,

2, Scriven Grove, Knaresborough.

Senior Science Master, King James's Grammar School, Knaresborough. M.A. Cambridge University. First Class, Part I, Natural Sciences Tripos, 1896; First Class, Part II, Natural Sciences Tripos, 1897 (with Chemistry as special subject). Author of "Equivalent Weight of Cyanogen" (*Proc. Chem. Soc.*, 1898, p. 174). Author of "The Atomic Weight of Nitrogen" (*Trans.*, 1900, p. 117).

G. D. Liveing.	H. J. H. Fenton.
W. J. Sell.	James Dewar.

Alexander Scott.

Eling, Thomas Henry James, B.A.,
32, Hill Top Avenue, Shepherd's Lane, Leeds.
Chemistry Instructor, Southern Higher Grade School, Leeds. Graduate of Oxford University, with Honours in Chemistry.

V. H. Veley.	J. E. Marsh.
W. W. Fisher.	J. Hembrough.

John Watts.

Hanson, Edward Kenneth,
Hadley Wood, N.
Student of Natural Science. First Class Natural Science Tripos, Part I, 1900. Desires admission in order to enjoy the advantages of membership, use of library, &c.

M. M. Pattison Muir.	H. J. H. Fenton.
S. Ruhemann.	W. T. N. Spivey.

R. S. Morrell.

Harry, Frederick Thomas,
106, Sandmere Road, Clapham, S.W.
Chemical Student. A three years' Chemical course at Finsbury Technical College, obtained Certificate, and am now engaged in Research at the Central Technical College.

Henry E. Armstrong.	William A. Davis.
Gerald T. Moody.	T. M. Lowry.

Edwin C. Jee.

Horton, Edward,
8, Orford Street, Chelsea, S.W.,
Chemical Student. I studied Chemistry for 3 years at Finsbury Technical College, obtaining the College certificate in 1900. Since October, 1900, I have been engaged in research work under Dr. Armstrong at the Central Technical College.

Henry E. Armstrong.	Edward W. Lewis.
Gerald T. Moody.	James Moir.
William A. Davis.	Sidney S. Napper.

Kiddell, Christopher George,
24, Queen's Gardens, Muswell Hill, N.
Science Master and Lecturer under Herts County Council. B.A.

W. B. Hards.	J. W. Shepherd.
Henry E. Armstrong.	*G. T. Morgan.*
M. O. Forster.	*James C. Philip.*

Lattey, Robert Tabor,
Trinity College, Oxford,
Student of Chemistry.
H. Brereton Baker. Allan F. Walden.
D. H. Nagel. Harold Hartley.
F. R. L. Wilson.

Lehmann, Adolf Ludwig Ferdinand,
Bangalore, Mysore, India.
Agricultural Chemist to Gov. Mysore. Graduate University of Toronto (B.Sc.), 1889. Assistant Chemist Central Experimental Farm, Ottawa, Canada, 1890—1893; Chemist La. Exp. Station, New Orleans, La., U.S.A., 1893—1894; Student Wislicenus, Leipzig, Germany (Ph.D.), 1894—1897. Dissertation "Dibenzoyldiphenylbutadiën and its Reduction to Tetraphenylbenzoyl" (*Annalen*, 302, p. 195). Lecturer on Organic Chemistry, Queen's University, Kingston, Canada, 1897—1899.
J. Walter Leather. W. H. Ellis.
Frank T. Shutt. *W. R. Lang.*
Frank G. Wait. *W. Lash Miller.*

Lowson, William,
83, Kyrle Road, Clapham Common, London.
Assistant Analyst in Government Lab. Six years' experience in Pharmacy and registered as Chemist under Pharmacy Act; three years' training at Yorkshire College, Leeds; B.Sc. (Lond.), A.I.C. Demonstrator in Chemistry at Yorks College.
T. E. Thorpe. John McCrae.
Arthur Smithells. Julius B. Cohen.
H. M. Dawson.

Macdonald, F. G.,
Government Laboratory, Durban.
Analytical Chemist and Assayer. Four years assistant chemist Roxburgh Sugar Refining Co., Greenock. Three years with Messrs. Tatlock and Readman, City Analysts, Glasgow, part of which time as a student and the remainder as an assistant. Two years Assayer to Durban Roodepoort Gold Mining Co., Transvaal, three years Cyanide Manager to the same company. At present in the Government Laboratory, Durban, as temporary assistant, as my services are still retained by the Durban Roodepoort G. M. Co.
E. Nevill. R. R. Tatlock.
Angus Smith. R. T. Thomson.
John Clark.

McLaren, Daniel, B.Sc.,

Brookdale, Grey Street, Stalybridge.

Science Teacher. Graduate in Science (Chemistry and Physics). St. Andrs. "Forrester Prizeman" (Chemistry). 2nd "Neil Arnott" Prizeman (Physics). Teacher of Chemistry since 1890. Principal and teacher of Chemistry, Technical School, Stalybridge.

Thomas Purdie. Albert Morris.
Joseph Brierley. Jas. Grant.
John Allan.

Oram, Frank,

Market Place, Romsey.

Pharmaceutical Chemist. Senior Medallist in Chemistry and Materia Medica.

W. B. Randall. *David Howard.*
J. Brierley. *Peter MacEwan.*
Harry Wilson. *Thomas Tyrer.*

Powell, John,

Balliol House, Wentworth Street, E.

Teacher of Physics at the Goldsmiths' Institute, New Cross. Am a B.Sc., London.

William J. Pope. A. W. Harvey.
Stanley J. Peachey. *M. O. Forster.*
Henry. A. Miers.

Purvis, John Edward,

University Chemical Laboratory, Cambridge.

Assistant to the Professor of Chemistry, Cambridge University. M.A. (St. John's College, Cambridge); Associate Royal College of Science (Ireland); Associate Institute of Chemistry.

G. D. Liveing. Alexander Scott.
James Dewar. H. J. H. Fenton.
W. J. Sell.

Russell, James Bertram,

356, Padiham Road, Burnley,

Schoolmaster. B.Sc. (Lond.). Late Scholar and Associate of University College, Cardiff. Formerly Lecturer in Chemistry for the County Council of Hertfordshire. Author of "Notes on Volumetric Analysis." For 5 years Senior Science Master, Grammar School, Burnley.

Claude M. Thompson. G. S. Turpin.
E. P. Perman. H. B. Dixon.
W. H. Perkin, jun.

Sandford, Thomas,

2, Market Place, Ulverston.

Analytical Chemist. Analytical Chemist to Messrs. Harrison, Ainslie and Co., Ltd., Ulverston, Charcoal iron makers and mines owners. Student under E. Richards, Esq., F.I.C., and F. B. Last, Esq., F.C.S.

Frank B. Last. Geo. R. Thompson.
Gilbert Howard Daniel. *Richd. Spencer.*
James E. Ferguson.

Sheppard, Samuel Edward,

Ravensmere, Bromley Road, Catford, S.E.

Student in the Chemical Department of University College, London. Passed Intermediate Examination in Science (Honours). Reading for B.Sc. (Honours) Examination at the London University.

William Ramsay. Edward C. Cyril Baly.
Morris W. Travers. Lionel M. Jones.
Charles M. Stuart.

Sichel, Gerald Theodore Sylvester,

R.N. Hospital, Haslar, Gosport.

Surgeon R.N. Assistant Instructor, &c., to Surgeons on entry into R.N. Lecturing and demonstrating in practical analytical work and on serum therapeutics since Feb. 1900. Admiralty analyses of water supplies of the service, foods, liquors, and general hygienic laboratory work since Feb. 1900. F.R.C.S. (Eng.); L.R.C.P. (Lond.); late H. S. Guy's Hospital.

Thos. Stevenson. Walter C. C. Pakes.
John Wade. William J. Pope.
Chas. Mills.

Smith, Andrew Biggam,

Queenstown, Cape Colony, S.A.

Analytical Chemist. Student of Chemistry in Andersonian College, Glasgow, under Prof. Henderson, D.Sc., from March 1892 to April 1895. For some time Chemist with the Scottish Oil and Chemical Co., Keppochhill, Glasgow, now with M. Armstrong, Chemist and Druggist, Queenstown, Cape Colony, South Africa.

G. G. Henderson. Thomas Gray.
James Robson. Matthew A. Parker.
A. Humboldt Sexton.

Spence, John Davidson,

2, Hawk Hill Place, Perth Road, Dundee.

Assistant Chemist and Assayer in the Muntz Metal Works, Birmingham. I was an assistant Chemist in the laboratory of Mr. G. D. Macdougald, F.I.C., Public Analyst of Dundee, for three years, and I am engaged in research work for the firm with whom I am at present engaged.

John S. Lumsden. James Walker.
John Foggie. *Jas. Braik Mason.*
Percy F. Frankland.

Tankard, Arnold Rowsby,

67, Surrey Street, Sheffield.

Analytical Chemist. Analytical and Literary Assistant to Mr. A. H. Allen. Undertaker of various investigations recorded in *Commercial Organic Analysis, Chemical News,* &c.

Alfred H. Allen. G. E. Scott-Smith.
P. J. Hartog. *J. F. Thorpe.*
George Young. *D. L. Chapman.*
Wm. A. Bone.

Tatam, George William Gerald,

Mercers' Hall, Cheapside, E.C.

Chemist in charge of the Laboratory and Gas Testing Department of the Gas Light and Coke Company's Nine Elms Station. I am a past student of the City and Guilds of London Institute, Finsbury, where I obtained the Diploma in the Department of Applied Chemistry.

Raphael Meldola. Ernest H. Roberts.
F. Southerden. Otto Hehner.
Greville Williams.

Whitton, William Arthur,

Bristol Brewery, Brighton.

Brewer. Two years pupil to H. E. Wright, Esq., F.C.S. Nine months pupil to Messrs. Matthews and Lott, Analytical Chemists. Two and a half years 2nd Brewer, Cheltenham Original Brewery Co. Ltd., now Brewer, Bristol Brewery, Brighton. Desirous of keeping myself informed in Chemical Science.

Herbert Edward Wright. Arthur A. Leon.
Chas. Geo. Matthews. *Jas. O'Sullivan.*
William Frew.

Whittle, James,
30, Bridge Street, Morpeth.

Chemist. Interested in Agricultural and Photographic Chemistry and desirous to obtain the Society's papers, &c.

William Mair.	Geo. F. Merson.
R. E. S. Richardson.	*Fredk. Gilderdale.*
Frank R. Dudderidge.	*John Gibson.*

Wilson, Duncan Randolph, B.A.,
Magdalen College, Oxford.

Lecturer in Natural Science at Magdalen College, Oxford. First Class in the Final School of Natural Science (Chemistry) at Oxford, 1898. *Publication.* Luther und Wilson, "Ueber das elektromotorisches Verhalten von Stoffen mit mehreren Oxidationsstufen" (*Zeitschr. f. physik. Chemie*, 1900, 488).

Henry A Miers.	W. W. Fisher.
V. H. Veley.	H. L. Bowman.
J. E. Marsh.	D. H. Nagel.
John Watts.	*A. Vernon Harcourt.*

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Issued 15/6/1901

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 239.

June 6th, 1901. Professor THORPE, C.B., F.R.S., Vice-President, in the Chair.

Messrs. Oldershaw, Martin, Jemmett, Dunstan, Bousfield, Taylor, Goltz, and Hyder were formally admitted Fellows of the Society.

The following Certificates were read for the first time:—Samuel Irwin Crookes, Thanet Street, Clay Cross, Chesterfield; Herbert Blackmore Hammond, 3 Vicar's Close, Lichfield; Christian Müller, 10 Selwyn Avenue, Richmond, S.W.; Rowland Samuel Potter, 2 Museum Hill, Haslemere; Robert Stephenson, jun., Burwell, Cambridgeshire; Frank Wade, 36 Craven Park, Harlesden, N.W.; Morton Wager, 5 Wilton Street, Batley.

Of the following papers, those marked * were read.

***93. "A laboratory method for the preparation of ethylene." By G. S. Newth.**

By substituting tribasic phosphoric acid for sulphuric acid in the ordinary process for obtaining ethylene, this gas may be prepared in a high state of purity. Syrupy phosphoric acid is boiled in a flask until the temperature reaches 200°, when ethyl alcohol is delivered drop by drop to the bottom of the boiling liquid. If the temperature is maintained about 220°, an abundant evolution of the gas takes place. As the liquid does not char or froth up, the operation may be conducted in a small reaction vessel; and as the gas is entirely free

from carbon dioxide, and of course from sulphur dioxide, it is not necessary to wash it.

The liquid products of the reaction, consisting of water, ether, unchanged alcohol, and a small quantity of an oily liquid, are collected in a vessel cooled by ice, the ethylene passing on practically pure.

By acting in a similar manner upon methyl alcohol, the gas evolved is pure methyl ether; from propyl alcohol, propylene is produced. In the case of the normal alcohol, a temperature about 250° is required to bring about the decomposition, whilst the secondary alcohol splits up rapidly at 210°.

***94. "Oroxylin." By W. A. H. Naylor and C. S. Dyer.**

The authors described the methods of isolation and purification of oroxylin, a yellow, crystalline substance obtained from *Oroxylum Indicum*.

Its chief decomposition product, through the action of caustic alkali of different strengths, is benzoic acid, but if the reagent be applied in the cold and in the form of a weak solution, the primary product is benzaldehyde. With bromine it forms a dibromo-derivative which crystallises in needles melting at 175°; on acetylation, a triacetyl derivative is obtained which crystallises in colourless needles melting at 150°. The authors conclude that oroxylin contains three hydroxyl groups, a loosely attached benzene nucleus, and they assign to it the formula $C_{19}H_{14}O_6$.

***95. "The constitution of the acids obtained from α-dibromocamphor." By A. Lapworth and W. H. Lenton.**

When tribromocamphonolactone (*Trans.*, 1900, 77, 458) is hydrolysed with alkali, and the product oxidised with cold sodium hypobromite, a mixture of acids is obtained from which trimethylsuccinic acid and a small quantity of camphoronic acid have been isolated. The greater portion of the mixture, however, consists of a dibasic lactonic acid, $C_9H_{12}O_6$, which has been identified with the acid hitherto known as β-hydroxycamphoronic acid.

The authors conclude that when bromocamphorenic acid is converted into α-monobromocampholid, the lactonic oxygen becomes attached to the ring at the δ-position with regard to the carboxyl group, instead of at the γ-position as was at first thought probable (*Trans.*, 1899, 75, 1139), the only possible formula for camphonic acid being $CO_2H\cdot CMe\langle\begin{matrix}CH_2—CH_2\\CMe_2\cdot CH_2\end{matrix}\rangle CO$. Bromocamphorenic acid and camphononic acid must be represented by the formulæ

$CO_2H\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\ CMe_2\cdot CH\end{matrix}>CBr$ and $CO_2H\cdot CMe<\begin{matrix}CH_2-CH_2\\ CMe_2\cdot CO\end{matrix}$ respectively.

The formulæ thus arrived at are in complete accordance with the properties of the compounds, and it is now easy to understand the great difference in the reactivities of the carbonyl groups of camphonic acid and camphononic acid. The change induced in α-dibromocamphor by moist silver compounds must be represented by the scheme

$$\begin{matrix}CH_2\cdot CH-CBr_2\\ |\quad\ CMe_2\quad |\\ CH_2\cdot CMe-CO\end{matrix} + H_2O = \begin{matrix}CH_2\cdot CBr:CH\\ |\quad\ CMe_2\\ CH_2-CMe\cdot CO_2H\end{matrix} + HBr,$$

and the authors suggest that an intermediate compound containing a trimethylene ring may be formed. Such an assumption is possibly applicable to many other changes in the camphor and terpene series, including the apparent migrations of methyl groups from one carbon atom to an adjacent one (a type of change otherwise without real analogy) and the formation of camphene derivatives from bornyl chloride and allied compounds (compare Marsh, *Proc.*, 1899, **15**, 54).

***96. "The decomposition of chlorates. IV. The supposed 'mechanical' facilitation of the decomposition of potassium chlorate." By W. H. Sodeau, B.Sc.**

The supposed analogy between the decomposition of potassium chlorate and the boiling of water, in respect of the facilitating action of certain powders, is invalidated by the fact of the former not being appreciably facilitated by reduction of pressure to 1 mm. (*Trans.*, 1900, **77**, 144). There would seem to be a possibility of chemical action with all substances known to produce a marked effect on the rate of decomposition of potassium chlorate.

From an experiment in which 1 per cent. of barium sulphate was added and a 500 per cent. increase of rate observed, Veley concludes that "chemically inert" powders facilitate the decomposition (*Phil. Trans.*, 1888, **179**, [A], 270).

The author has studied the effect of adding 1 per cent. of barium sulphate, and finds that the average increase of rate amounts to only 16 per cent. There is evidence of the formation of a little barium chlorate by double decomposition, and this would appear to account for the slight facilitation observed.

It is concluded that the supposed ability of chemically inert solid particles to facilitate the decomposition of potassium chlorate is unsupported by experimental evidence, and, if actually existent, is inadequate to explain even a small fraction of the effect of the oxides

of manganese, iron, cobalt, nickel, and copper. The action of these latter substances would, therefore, appear to be entirely chemical.

*97. "On the action of sodium methoxide and its homologues on benzophenone chloride and benzal chloride." By J. E. Mackenzie, D.Sc., Ph.D.

The author has already (*Trans.*, 1896, **69**, 985) described the preparation of dimethoxy-, diethoxy-, and dibenzoxy-diphenylmethanes by the action of sodium meth-, eth-, and benz-oxide respectively on benzophenone chloride. To these are now added, *dipropoxydiphenylmethane*, $(C_6H_5)_2C(OCH_2{\cdot}CH_2{\cdot}CH_3)_2$, colourless, prismatic crystals, m. p. 33—34·5°; *diisobutoxydiphenylmethane*, $(C_6H_5)_2C[OCH_2{\cdot}CH(CH_3)_2]_2$, m. p. 36—38°, readily splitting up in accordance with the equation $(C_6H_5)_2C[OCH_2{\cdot}CH(CH_3)_2]_2 = (C_6H_5)_2CO + [(CH_3)_2CH{\cdot}CH_2]_2O$; *4 : 4'-dihydroxytetraphenylmethane*, $(C_6H_5)_2C(C_6H_4OH)_2$, which is formed instead of the diphenoxy-compound, $(C_6H_5)_2CCl_2 + 2C_6H_5ONa = (C_6H_5)_2C(C_6H_4OH)_2 + 2NaCl$, crystallises from ethereal solution with two molecules of ether of crystallisation, and melts at 285—287°. It gives a *diacetate*, $(C_6H_5)_2C(C_6H_4OCH_2CO)_2$, m. p. 170—171°. Experiments on the action of ethyl alcohol and of 1 per cent. alcoholic solution of hydrochloric acid on benzophenone gave negative results.

Nitration of dimethoxydiphenylmethane resulted in the formation of 4 : 4'- and 3 : 3'-dinitrobenzophenones, whilst aniline split it up, forming diphenylmethylene anilide.

The action of sodium methoxide, ethoxide, and benzoxide on benzal chloride at the ordinary pressure was tried. The first and second actions proceed as described by Wicke (*Ann.*, 1857, **102**, 356), dimethoxy- and diethoxy-benzylidene being formed. From the benzoxide experiment the only substance isolated was stilbene. By heating phenol itself with benzal chloride, condensation took place as follows, $C_6H_5{\cdot}CHCl_2 + 2C_6H_5OH = C_6H_5{\cdot}CH(C_6H_4OH)_2 + 2HCl$, the substance formed being identical with 4 : 4'-dihydroxytetraphenylmethane (*Ber.*, 1889, **22**, 1944), and giving the same diacetyl derivative.

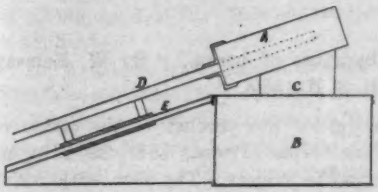
When similar experiments were made under pressure, the action was found to be quite different from the above, and may be expressed generally thus: $R'ONa + C_6H_5{\cdot}CHCl_2 = R'Cl + C_6H_5{\cdot}CHO + NaCl$. In this manner, methyl, ethyl, propyl, and benzyl chlorides were obtained.

When sodium ethoxide acts on ethylene dibromide under pressure, acetylene is produced.

***98. "A kerosene oil blowpipe." By A. Richardson, Ph.D.**

This blowpipe has been devised in order to utilise the combustion of kerosene oil for the production of a blowpipe flame, suitable for glass blowing and other purposes, so as to combine the advantages of a gas blowpipe while independent of a supply of gas. The need of such a blowpipe is obvious in a country like India, where gas is not always available, and where in many college laboratories not supplied with gas blowpipe work is necessarily limited to operations with the mouth blowpipe and spirit lamp.

At first it seemed possible to use one of the vegetable oils, such as cocoanut oil, by burning it in a modified form of glass blower's "tallow lamp," but the tendency of all such oils to char at the temperature of the blowpipe flame renders them useless as a continuous source of heat unless the wick is being constantly trimmed. As kerosene oil does not char, it was selected for this purpose; its combustion, however, in a lamp without a chimney requires special arrangements if it is to give a solid, steady, flame, easily regulated and completely under control of the operator, and it was only after many unsuccessful attempts that a lamp was constructed which fulfils all the requirements of the case.



As it now stands, the blowpipe consists of a metal tube, *A*, 1½ inches long and ¾ of an inch in diameter, fixed at an acute angle above the oil holder, *B*, with which it is connected by a flattened tube or wick holder, *C*. A wick about 1 inch wide passes from *B* through *C*, round the inside of *A*, and back to *B*, leaving the central portion of the tube open. The wick is protected and kept in its place by a tube of iron wire gauze projecting beyond the wick on either side. The lower end of *A* is closed by a perforated cap, through the centre of which the blowpipe jet, *D*, passes. This is made to slide backwards and forwards on the rail, *E*, so that its position in the centre of the tube can be regulated.

A thread of asbestos dipping in the oil passes up the wick-holder and projects just in front of the wick at the open end of *A*.

To use the lamp the asbestos thread is first lighted, this furnishes a

small flame at the mouth of *A*; if now the bellows be worked, combustion takes place within *A* on the surface of the gauze. The size of the flame depends on the position of the jet, since combustion is practically limited to that portion of the wick exposed to the air current, thus when the jet is pushed up to the open end, a fine-pointed flame is produced; as it is drawn back into the tube, the flame increases in size, giving a roaring flame when the whole length of the wick is exposed. On stopping the air supply the flame immediately subsides to its original size, and burns quietly at the mouth of the tube. In this way the flame is under complete control, and gives no trouble when not in use.

Experience has shown that the wick remains in good condition for a long time; in one case it was found to be only superficially blackened after the blowpipe had been in use for several weeks.

The dimensions given above are those which the author has found most useful for general purposes, but with a wick 2 inches wide, contained in a tube of 1 inch bore, a much larger and [more powerful flame is obtained, suitable for large pieces of glass blowing, although it is not so easily regulated for the production of a small flame.

The efficiency of the blowpipe has been proved by long use; with its aid all the ordinary glass blowing which before was out of the question without gas may be done.

***99. "Preliminary note on hydrides of boron." By W. Ramsay and H. S. Hatfield.**

Since Jones and Taylor investigated the product of the action of hydrochloric acid on magnesium boride (*Trans.*, 1881, 39, 213), no work seems to have been done on the subject. The ease with which gases can be liquefied and solidified by means of liquid air made it probable that an attempt to isolate boron hydride by cooling the gas from magnesium boride would be successful.

The magnesium boride obtained for the first experiment was made by heating together boron trioxide and magnesium powder in a wrought-iron crucible on an ordinary fire. The friable, black mass, treated with concentrated hydrochloric acid in a vacuous flask, gave off a gas which, when passed through a cooled wash-bottle, deposited white crystals. The hydrogen remaining in the bulb was completely removed by pumping, and on allowing the solid material to warm up it gasefied, and was collected separately. It liquefied before gasefying, and yielded about 50 c.c. of a colourless gas. The gas had a strong, fœtid odour, and burned with a bright green flame.

Its density was 19·36; for a bulb of 32·04 c.c. capacity contained 0·0432 gram of the gas at 605·9 mm. pressure and 12·2°. When sparks

were passed through the gas, it was decomposed, a filament of boron joining the electrodes and conducting the current. It was found most convenient to commence the operations with a jar and spark-gap interposed, and when considerable decomposition had taken place to finish up with an "electric flame," that is, removing the Leyden jar. With the intermittent spark, the filaments were ruptured and fell; and with gas largely decomposed, they were no longer formed.

A quantitative experiment showed that the increase of volume, on decomposition, was from 2 to 3; for 19·1 c.c. of gas at 12° increased, after decomposition, to 28·1 c.c. at 11·5°. The ratio between these numbers is 2 to 2·94. This sample of gas had been exposed to the action of solid potassium hydroxide for 12 hours; it had previously passed over soda lime and phosphoric anhydride. An attempt was made to collect the boron which separated out from another sample of 26·8 c.c. on decomposition, but it was not possible to collect it free from mercury. However, it was washed out by help of ether, the ether was removed by evaporation, and the mercury was distilled off in a current of hydrogen. The residue weighed about 0·05 gram, a number not greatly differing from 0·045, the weight of the gas. The experiment was a difficult one, and could not be expected to furnish very accurate results.

These experiments render it probable that the gas consisted mainly of a compound, B_2H_2. This gas is practically insoluble in water; it is fairly stable.

The hydrogen which passed through the cooled wash-bottle burned with a green flame; a porcelain lid held in the flame was not stained with boron, as stated by Jones and Taylor. Even when the gas was passed through a red hot glass tube filled with fragments of unglazed clay, it still burned with a green flame, and the white clay was hardly stained. A quantity of the uncondensable gas was collected in a vacuous receiver (for it appeared to be somewhat soluble in water), and it was concentrated by diffusion through tobacco-pipe stems. Several hundred c.c. of the diffused gas were passed through a vessel, cooled by liquid air boiling under low pressure, and the gas was subjected to a pressure of 2 atmospheres, so as to reduce the volume occupied by the diluent hydrogen. A small amount solidified, but it was not possible to reduce the pressure much without its volatilising. The density of this sample of gas was 2·59, for 32·04 c.c. at 16·5° and 758·6 mm. weighed 0·0071 gram. On the assumption that its formula is BH_3, 26·5 per cent. of the sample consisted of that gas; the remainder was hydrogen. Of this mixture, 7·45 c.c. were sparked for 2 hours, and deposited boron on the platinum electrodes. The volume after sparking was 8·50 c.c., an increase of 1·05 c.c. Now, 26·5 per cent. of 7·45

is 1·97; hence the increase of volume was in the ratio 1·97 : 3·02, a sufficiently close approximation to 2 : 3.

Other attempts to prepare the compound B_2H_2 have not been so successful. The condensable gas has, up to now, consisted of a compound decomposable with increase of volume on addition of solid potassium hydroxide, or of concentrated sulphuric acid. The density of this sample was found to be 18·1, for the weight of 32·01 c.c. measured at 16·4° and 479·0 mm. was 0·0187. It also deposited what appeared to be boron on sparking. There appear, therefore, to be two compounds of the formula B_2H_2, one relatively stable, the second unstable and easily changed by reagents. The yields in the last case have been very poor, and the authors have not yet secured the conditions for producing the stable compound with certainty, uncontaminated by the unstable gas.

If it may be permitted to speculate regarding the hydrides of boron it is probable that the following are capable of existence:

BH_3.	$H_2B{-}BH_2$.	$H_2B{-}BH{-}BH_2$.	Saturated.
	$HB{=}BH$.	$H_2B{-}B{=}BH$.	Unsaturated.
			cyclo-Saturated.
			cyclo-Unsaturated.

The authors are inclined to suspect that the stable compound of the formula B_2H_2 is the *cyclo*-compound, to which the name *cyclo*triborene appears applicable; it is possible that triborene is the unsaturated compound, of which the formula is given above. The last formula given is the hydrogen analogue, in all probability, of the calcium, strontium and barium borides described by Moissan and Williams (*Compt. rend.*, 1897, 125, 629).

The residues left after treatment of the magnesium boride with acid, when washed and dried, give off torrents of gas on being heated; this gas consists, for the most part, of hydrogen, and contains only a trace of boron. It no doubt results from the decomposition of solid hydroborons, but the authors have not yet succeeded in separating them from the boron with which they are mixed.

100. "On some relations between physical constants and constitution in benzenoid amines. Part II." By P. Gordan and L. Limpach.

By the substitution of the benzenic hydrogen in formyl and acetyl anilides by methyl groups 38 compounds can be obtained. These

compounds may be arranged, or classified, according to the number ρ of the substituting groups and also according to their relative positions —isomerides. The mode of dependence of their melting points may be seen by comparing their experimentally determined values. The mean, D, of the melting points of an isomeric series may be calculated from ρ. In each isomeric series there is at least one member the melting point of which is identical with the mean value or differs very little from it. The melting points of the others differ evenly in two directions (higher or lower) from D, and in such manner that where one compound has a melting point considerably above D, another compound, of the same series, has a melting point as much below D. For instance, in the acet-toluide series the mean D = 106·5. This is practically, the melting point of 1 : 2-acet-toluide (107°). The 1 : 3-compound melts at 65·5° and the 1 : 4 at 147°, the latter compound therefore melting 40·5° higher and the 1 : 3, 41° lower than the mean D.

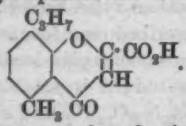
The melting points are higher when both ortho-positions are occupied and lower when meta- or meta- and para-positions are occupied. The melting point seems to be mainly determined by the ortho- or neighbouring position. This observation or view is borne out by the theory of "invariants."

101. "Condensation of phenols with esters of the acetylene series. V. Homologues of benzo-γ-pyrones." By S. Ruhemann.

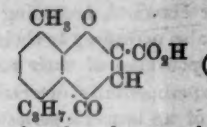
In continuation of his research, the author has studied the behaviour of the esters of chlorofumaric and phenylpropiolic acids towards thymol and carvacrol, and thus obtained the following compounds.

Ethyl β-thymoxycinnamate, $C_6H_5\cdot C(O\cdot C_6H_3<^{C_3H_7\,(2)}_{CH_3\,(5)})\cdot CH\cdot CO_2Et$ (1), the corresponding *acid* (which decomposes at 138°), and *β-thymoxystyrene*, $C_6H_5\cdot C(O\cdot C_6H_3(CH_3)(C_3H_7))=CH_2$.

The product of the action of thymol on ethyl chlorofumarate, *ethyl thymoxyfumarate*, yields on hydrolysis the *acid* (m. p. 215° with evolution of gas) which is condensed by strong sulphuric acid to 5-*methyl*-8-*propyl*-1 : 4-*benzopyrone*-2-*carboxylic acid*,



Ethyl carvacroxyfumarate, formed from carvacrol and ethyl chlorofumarate, on hydrolysis yields the corresponding *acid*, which is transformed by strong sulphuric acid into 5-*propyl*-8-*methyl*-1 : 4-*benzopyrone*-

2-*carboxylic acid*,  (m. p. 237—238° with decomposition. This, on heating, loses carbon dioxide, and yields *propylmethyl*-1 : 4-*benzopyrone* (m. p. 59—60°).

102. "Gum tragacanth." By C. O'Sullivan.

The proximate constituents of the gum have been isolated, and the following were described:

Cellulose.—The constituent insoluble in boiling water and cold dilute acid and alkalis. Treated with boiling dilute sulphuric acid, it yields arabinose and a residue of a cellulosic nature still. This residue on further treatment with ammonia and bromine gradually dissolves, leaving no residue of normal cellulose.

Soluble Gum.—A series of gum acids of the nature of the geddic acids were prepared. They are lævorotatory, however, the rotation being about as much to the left as that of the geddic acids is to the right. The acids are shown to be polyarabinan-trigalactan-geddic acids, the chief of them being $11C_{10}H_{18}O_8,3C_{12}H_{20}O_{10},C_{23}H_{36}O_{20},H_2O$. The optical activity of this acid is $[\alpha] = -88°$. Its barium salt yields 3·29 per cent. BaO, against 3·23 per cent. required. On sulphuric acid hydrolysis, it should yield 71·7 per cent. arabinose. Quantities varying between 72 and 76 per cent. moderately pure arabinose were obtained from the mixed gum acids.

Granules.—The granules, apparently starch-granules, are coloured blue by iodine, and on treatment with diastase yield dextrose, but not maltose.

Nitrogenous Matter.—No attempt was made to purify this substance. It is of much the same nature as the nitrogenous matter described in dealing with the geddic gum (*Trans.*, 1891, **59**, 1061), but it does not give the same proteid reaction as that substance does.

Bassorin was not completely purified, but it was found to be an acid having $[\alpha]_D = +98°$; the neutral barium salt contains 9·2 per cent. BaO. Under the action of excess of alkalis it yields two acids, α- and β-tragacanthan-xylan-bassoric acid. The nature of this transformation will be described on a future occasion.

α-Tragacanthan-xylan-bassoric Acid.—Its preparation and purification were described; it is soluble in cold water. Its analysis led to the formula $C_{24}H_{24}O_{20},H_2O$. $[\alpha]_D = +138·6°—138·2°$; $D = 4·12—4·13°$. Barium, calcium and silver salts were prepared; the silver salt is the most insoluble, the calcium salt least. The neutral barium salt gave 19·21 per cent. BaO, the calcium salt 8·24 per cent. CaO, and the silver

salt 22·2 per cent. Ag. $C_{24}H_{34}O_{20},BaO$, requires 19·24 per cent. BaO, the calcium salt 8·02 per cent., and the silver salt 24·77 per cent. In consequence of decomposition it was not possible to prepare the silver salt with any degree of satisfaction.

Digested for 20 minutes at 98° with 5 per cent. sulphuric acid, it yields a lævorotatory pentose, *tragacanthose*, $[\alpha]_D = -30°$ approx., and *xylan-bassoric acid*, $[\alpha]_D = +200°$, the barium salt yielding 22·5 per cent. BaO. The equation

$$\underset{}{C_{24}H_{38}O_{21}} + H_2O = \underset{\text{Tragacanthose.}}{C_5H_{10}O_5} + \underset{\text{Xylan-bassoric acid.}}{C_{19}H_{28}O_{17}}$$

represents the hydrolysis. $C_{19}H_{26}O_{16}O_{16},BaO$ requires 23·07 per cent. BaO.

Xylan-bassoric acid is almost insoluble in cold water, the alkaline salts are soluble, salts of the alkaline earths and most heavy metals are insoluble. Acted upon with 5 per cent. sulphuric acid, *xylose* and *bassoric acid* are obtained.

$$\underset{}{C_{19}H_{28}O_{17}} + H_2O = \underset{\text{Xylose.}}{C_5H_{10}O_5} + \underset{\text{Bassoric acid.}}{C_{14}H_{20}O_{13}}$$

Bassoric acid is almost insoluble in cold water; in alkaline solution its optical activity was found to be $[\alpha]_D = +255°$, and the barium salt yielded 28—29 per cent. BaO. $C_{14}H_{18}O_{12},BaO$ requires 28·8 per cent. BaO.

β-Tragacanthan-xylan-bassoric acid is left behind as a crumbly mass, when the *α*-acid is dissolved out by cold water. On combustion it yields the same numbers as the *α*-acid. In alkaline solution $[\alpha]_D = +163°$—$164°$. The barium and calcium salts, as well as most of the salts of the heavy metals, are of very low solubility. Treated with sulphuric acid, it yields the same products as the *α*-acid.

In a future paper, the author hopes to be able to describe bassorin more fully, as well as its conversion into the two acids described, also the two acids themselves, and particularly the products of their hydrolysis, the sugar tragacanthose, and the final acid, bassoric acid.

103. "Optically active dimethoxysuccinic acid and its derivatives." By T. Purdie, F.R.S., and J. C. Irvine, B.Sc.

By alkylating methyl, ethyl, and propyl tartrates by means of silver oxide and methyl iodide, the authors have obtained the corresponding optically active dimethoxysuccinates. The methyl ester is crystalline (m. p. 51°, $[\alpha]_D^{20°} = +82·52°$); the ethyl and propyl esters are liquids, giving $[\alpha]_D^{20°} = +89·96°$, $[\alpha]_D^{20°} = +85·39°$ and $[\alpha]_D^{20°} = +84·92°$, $[\alpha]_D^{20°} = +81·06°$ respectively. Dimethoxysuccinic acid is crystalline (m. p. about 151°), and gives in aqueous solution of varying concentration $[\alpha]_D^{20°} = +72·28°$ to $76·63°$, in acetone $+89·29°$ to $95·80°$. The optical

activity of aqueous solutions of the diamide and of various metallic salts has also been examined.

Certain regularities in the relations of the rotations of ethereal mono- and di-alkyloxysuccinates and of the corresponding acids and metallic salts were discussed, as well as Frankland's views (*Trans.*, 1899, 75, 347) concerning the probable cause of the maximum specific rotation exhibited by the series of ethereal malates and lactates.

104. "The influence of solvents on the optical rotation of ethereal dimethoxysuccinates and tartrates." By T. Purdie, F.R.S., and W. Barbour, M.A., B.Sc.

To determine whether any change of configuration is produced by alkylating the tartaric esters with silver oxide and alkyl iodide, tartaric acid was regenerated from dimethoxysuccinic acid by heating the latter with hydriodic acid; *d*-dimethoxysuccinic acid yielded *d*-tartaric acid.

The rotations of methyl, ethyl and propyl dimethoxysuccinates in water, methyl alcohol and benzene at varying concentrations were determined, and for purposes of comparison some observations were made on solutions of the corresponding tartrates; the latter were not proceeded with further, so as to avoid interference with the work of T. S. Patterson (*Trans.*, 1901, 79, 167, 477). In general the rotations of the former esters are influenced less by solvents than those of the latter, and in most cases the action is oppositely directed.

The authors pointed out that the direction of the effects of a solvent on the rotations of the members of a homologous series is often reversed on ascending the series, and they connect this with the corresponding reversed effect of the addition of CH_2 to successive terms.

From molecular weight determinations of the esters in water and benzene, more particularly from the results obtained with benzene solutions of the tartrates, the conclusion is drawn that the aggregation of disymmetric molecules is not a predominant factor in the influence of solvents on rotation.

To ascertain whether their observations support the theory of Patterson (*loc. cit.*) on the connection between rotation and molecular solution volume, the latter constants were calculated for a number of the solutions examined, but the results are inconclusive. In addition to the factors pointed out by Patterson which may mask this connection, the authors suggest another phenomenon, probably of frequent occurrence, which they think may interfere with the relationship in question.

ADDITIONS TO THE LIBRARY.

I. Donations.

Reports of the Royal College of Chemistry and Researches conducted in the Laboratories in the years 1848—49—50—51. Vol. II. London 1853. From John Spiller, Esq.

Bolton, H. Carrington. A select bibliography of chemistry. 1492—1897. Section VIII.—Academic dissertations. Washington 1901. From the Smithsonian Institution.

II. By Purchase.

Lassar-Cohn. Arbeitsmethoden für organisch-chemische Laboratorien. Allgemeiner Teil. Third edition. Leipzig 1901.

Museum Hermeticum, continens tractatus chymicos novem præstantissimos. Ill. Frankfort 1625.

Proceedings of the Philosophical Society of Glasgow, volume I 1841—1844.

Pamphlets.

Schaer, Ed. C. F. Schönbein's Untersuchungen über die Polarisation des Sauerstoffs. Leipzig 1901.

British Association for the Advancement of Science. Report of the Committee on the bibliography of spectroscopy. London 1894.

Madan, H. G. Lecture demonstrations of the laws of polarised light. London 1899.

Baker, R. T. On some new species of eucalyptus. (From the *Proc.* of the Linnean Society of N.S.W., 1900).

At the next meeting, on Thursday, June 20th, there will be a Ballot for the Election of Fellows, and the following papers will be communicated:—

"The direct union of carbon and hydrogen. Part II." By W. A. Bone and D. S. Jerdan.

"Ammonium and other imidosulphides." By E. Divers and M. Ogawa.

"Nitrilosulphates." By E. Divers and T. Haga.

"The decomposition of hydrocarbons at high temperatures." By W. A. Bone and D. S. Jerdan.

"The sugars from cellulose." By H. J. H. Fenton.

"On a theory of chemical combination." By G. Martin.

"On the occurrence of paraffins in the leaf of tobacco." By T. E. Thorpe, C.B., F.R.S., and John Holmes.

"Studies in the camphane series. Part IV." By M. O. Forster.

"On the decomposition of carbon dioxide, when submitted to electric discharge at low pressures." By J. N. Collie, Ph.D., F.R.S.

"Two new substances in lemon oil." By H. E. Burgess.

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June 20th, 1901. Professor EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

Messrs. Jordan, Blake, Eyre and Shutt were formally admitted Fellows of the Society.

The following Certificates were read for the first time:—Thomas Thorne Baker, 28, Church Road, Forest Hill, S.E.; Edwin Hobson, 3, Oxford Road, Liscard, Cheshire; Charles Harold Johnson, Beaumont, Northcote, Melbourne, Victoria, Australia; Edward Hall Miller, Common Hall, Hadleigh, Essex; Herbert Simpson Newbould, Trinity Hall, Cambridge; Allan Sandford, Market Place, Ulverton.

The PRESIDENT announced that Dr. Armstrong had undertaken to deliver the Frankland Memorial Lecture on Thursday, October 31st, 1901.

ADDRESS TO GLASGOW UNIVERSITY.

The following Address was presented to the University of Glasgow on the occasion of the four hundred and fiftieth anniversary of its foundation:—

"The Chemical Society, as representing Chemical Science in the United Kingdom, desires to congratulate the University of Glasgow on the celebration of the Four Hundred and Fiftieth Anniversary of its foundation.

"The Chemical Society recalls with pride the fact that Members of the University of Glasgow have been most distinguished Fellows, and

have contributed by their labours, some of which are among the classics of our Science, to the development of chemical learning.

"Thomas Graham, one of the Founders of our Society and our first President, was the most illustrious of the pupils of Thomas Thomson, whose name is honourably connected with Chemistry as head of one of the first Schools of Practical Chemistry established in this Kingdom, a school which he inaugurated within your walls.

"Thomas Anderson, an honoured name with you as a teacher, who was among the earliest to cultivate with an energy and zeal eminently characteristic the newly developed domain of Organic Chemistry, was for many years one of the most active of our Fellows.

"We sincerely trust that your University may continue to flourish in the future as in the past, and that its efforts to foster and promote the Science which we represent may be as successful in the years to come as they have been since the days of Black.

J. EMERSON REYNOLDS, *President.*
WILLIAM A. TILDEN, *Treasurer.*
WYNDHAM R. DUNSTAN,
ALEXANDER SCOTT,
RAPHAEL MELDOLA, } *Secretaries.*"

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Ormsby Gore Adams, Guy Ashwell, Thomas Aspinall, William George Aston, Hubert Haigh Barker, Edwin Sloper Beaven, Fred Bedford, Joseph Samuel Bridges, B.Sc., Arthur Crabtree, George Dean, M.A., Thomas H. J. Eling, B.A., Edward K. Hanson, B.A., Frederick Thomas Harry, Edward Horton, Christopher G. Kiddell, B.A., Robert Tabor Lattey, B.A., Adolf L. F. Lehmann, B.Sc., Ph.D., William Lowson, B.Sc., F. G. Macdonald, Daniel McLaren, B.Sc., Frank Oram, John Powell, B.Sc., John Edward Purvis, M.A., James Bertram Russell, B.Sc., Thomas Sandford, Samuel Edward Sheppard, Gerald T. S. Sichel, Andrew Biggam Smith, John Davidson Spence, Arnold Rowsby Tankard, George William G. Tatam, William Arthur Whitton, James Whittle, and Duncan R. Wilson, B.A.

Of the following papers, those marked * were read.

***105. "The direct union of carbon and hydrogen. Part II." By W. A. Bone and D. S. Jerdan.**

The authors have already shown (*Trans.*, 1897, 71, 41) that carbon and hydrogen combine at 1200°, forming a saturated hydrocarbon; and also that when the electric arc is passed between carbon terminals

in an atmosphere of hydrogen, a saturated hydrocarbon is produced in addition to acetylene, the formation of each continuing until a definite equilibrium between acetylene, the saturated hydrocarbon, hydrogen, and carbon vapour is established. It was then provisionally assumed that the saturated hydrocarbon produced both at 1200° and in the arc is methane.

Further experiments have been made in which the saturated hydrocarbons in question have been separated from the large excess of hydrogen (by means of palladium), and also, in the case of the arc gases, from the acetylene simultaneously produced. Analyses of the residual saturated hydrocarbons, mixed with whatever nitrogen was contained in the original hydrogen employed, have shown that whereas the gas obtained by the direct action of hydrogen upon solid carbon at 1200° consists of methane only, the saturated hydrocarbons produced in the arc consist of methane with one of its homologues, which further investigation has shown to be ethane.

The authors are able to show further that in the arc methane and ethane are produced simultaneously, and at rates which bear a constant ratio to one another throughout an experiment, until a definite equilibrium is reached. By calculation from the results of the previous experiments, interpreted in the light of later work, the proportions between the various hydrocarbons and hydrogen when this equilibrium is attained are shown to be:

Hydrogen	90 to 91 per cent.
Acetylene	8 to 9 „
Methane	1·25 „
Ethane	0·25 „

***106. "Ammonium and other imidosulphites." By E. Divers and M. Ogawa.**

The authors have already called attention to the occurrence of ammonium imidosulphite amongst the products of the decomposition of ammonium amidosulphite, and have given some account of the salt (*Proc.*, 1900, **16**, 113). They now separate it by dissolving it out with warm 90 per cent. alcohol, after having used 95 per cent. alcohol to extract some other crystalline matter and the red substance. By working in this way, the imidosulphite is obtained at once almost pure, requiring only to be washed with alcohol. It forms minute, very thin, glistening prisms, somewhat deliquescent, neutral to litmus and of mild sulphurous taste. Heated in the dry state, most of it decomposes, but a little occurs in the sublimate along with pyro-

sulphite. The residue left on heating it up to 150° consists of sulphur, sulphate, and imidosulphate. The salt is very soluble in water, and slowly decomposes in solution. Boiled with hydrochloric acid, it yields sulphur, sulphur dioxide, and amidosulphuric acid, the sulphur and sulphur dioxide representing, no doubt, decomposed thiosulphate, $2NH(SO_2NH_4)_2 + OH_2 = 2NH_2SO_3NH_4 + S_2O_3(NH_4)_2$. Ammonium imidosulphite gives a barium precipitate soluble in hydrochloric acid. Potassium imidosulphite and barium ammonium imidosulphite have been prepared, and are crystalline soluble salts.

*107. "Nitrilosulphates." By E. Divers and T. Haga.

Ammonium nitrilosulphate cannot be obtained by the sulphonation of ammonia, for the imidosulphate which is the product of the union of sulphur trioxide with ammonia is decomposed by heat only at a very high temperature, and then is radically broken up without giving any nitrilosulphate. The sulphonation of a nitrite first into hydroximidosulphate and then into the nitrile is therefore the only way open. The ammonium and potassium salts were obtained by Fremy (1845), and a potassium sodium salt, $SO_3Na{\cdot}N(SO_3K)_2$, by Raschig (1887). The ammonium salt, as it has the composition of $4NH_3 + 3SO_3$, is a very interesting salt, the existence of which had been forgotten. Sodium nitrilosulphate is so very soluble that it has not been isolated before. It can be obtained by passing sulphur dioxide into the most concentrated solution possible, containing sodium nitrite and sodium carbonate in the ratio of two molecules of the former to three of the latter salt, until the new salt begins to crystallise out. It occurs in small, sparkling, short, thick prisms containing $5H_2O$, and is exceedingly unstable. It is neutral to litmus. By dissolving the salt in concentrated, faintly alkaline solution of barium chloride, a precipitate is obtained, flocculent at first, but becoming crystalline and dense, of barium or barium sodium nitrilosulphate.

*108. "The decomposition of hydrocarbons at high temperatures. Preliminary note." By W. A. Bone and D. S. Jerdan.

For some months past the authors have been studying the decomposition of various hydrocarbons at a temperature of about 1150°. Since methane is the only hydrocarbon produced by the direct combination of carbon and hydrogen at 1200°, it seemed probable that any hydrocarbon would, at this temperature, be decomposed, yielding ultimately carbon, hydrogen, and a small percentage of methane. So far the authors have only studied the decomposition of methane and

acetylene in detail, but the recent publication of a paper "Ueber pyrogenetische Reactionen organischer Substanzen" by W. Ipatiew (*Ber.*, 1901, **34**, 596), in which he announces his intention to investigate the decomposition of hydrocarbons at high temperatures, makes it desirable that they should publish this note.

The method adopted by the authors, which will be described in detail in a future communication, consists in admitting the pure hydrocarbon into a vacuous, glazed porcelain tube (length 60 cm., internal diameter 12 mm., capacity about 65 c.c.), nearly the whole length of which has been previously heated to about 1150° in a specially designed Fletcher furnace. The experimental tube is properly jacketed so as to prevent any diffusion of furnace gases into it. The temperature, which can be maintained practically constant for several hours, was ascertained by means of a Roberts-Austen electrical pyrometer. After the gas under investigation has been subjected to the high temperature for a definite time, it is quickly pumped out into tubes over mercury.

Acetylene is very rapidly decomposed at 1150°; after one minute not more than 10 per cent., and after five minutes only a mere trace of it remains. Considerable quantities of a saturated hydrocarbon, which subsequent examination has shown to be methane, are formed during the early stages of the decomposition, and afterwards this methane is slowly, though never completely, resolved into its elements. Neither benzene nor ethylene are formed at any stage of the decomposition, and, after the final disappearance of acetylene, the gaseous products contain hydrogen and methane only. Carbon is liberated during the early stages as 'lamp-black,' which doubtless arises from the rapid decomposition of the acetylene, but afterwards it is only deposited on the inner surface of the tube in a form much resembling 'gas carbon.'

The following figures show the percentage composition of the gases obtained in a series of experiments in which the time of heating varied from 1 minute to 3 hours:

Time	1 min.	5 mins.	15 mins.	1¼ hours.	3 hours.
Acetylene	10·0	trace	nil	nil	nil
Methane	16·0	21·5	16·0	7·75	3·0
Hydrogen	74·0	88·5	84·0	92·25	97·0

Methane is resolved into its elements at 1150° more rapidly than would be generally supposed. The decomposition, however, only occurs at the surface of the containing tube, where the carbon is deposited in a form much resembling 'gas carbon' in appearance. At no stage of the decomposition was it possible to detect the formation of acetylene, ethylene or any other unsaturated hydrocarbon. A careful examination of the gas left after 15 minutes' heating has shown that it contains no other saturated hydrocarbon then methane. The following

figures indicate the percentage composition of the gas obtained at the end of 5, 15, and 30 minutes respectively, leaving out of the reckoning any small amount of nitrogen it contained :

Time.....	5	15	30 minutes.
Methane	37·5	12·25	6·6
Hydrogen.....	62·5	87·75	93·4

The authors are now completing a series of experiments on ethane, and then propose to extend the research to other typical hydrocarbons, and to temperatures other than 1150°.

***109 "Note on the sugars from cellulose." By Henry J. H. Fenton.**

In several previous communications (Fenton and Gostling, *Trans.*, 1898, **73**, 554; 1899, **75**, 423; 1901, **79**, 361, 807) it has been shown that various forms of 'cellulose' (such as filter paper and cotton) give considerable yields of the chloro- or bromo-derivatives of methylfurfural when they are heated with dry hydrogen chloride or bromide dissolved in an appropriate solvent. It was further shown than the formation of the bromo-derivative in any notable quantity is indicative of the presence of a *ketohexose* nucleus or grouping, and the existence of one or more such groupings in 'cellulose' was consequently inferred. Recent experiments indicate that the same observations apply also to the *chloro*-derivative.

After treatment of cellulose in this manner with dry hydrogen chloride and complete removal of the methylfurfural derivative by washing repeatedly with ether, a dark brown residue is left which, in the case of filter-paper, still shows a fibrous structure and amounts to about 90 per cent. of the material taken. If this residue is digested with warm water, a solution is obtained which gives all the reactions of *dextrose*. It is strongly dextrorotatory and with phenylhydrazine acetate, on heating, yields *glucosazone* (m. p. 204—206°. N = 15·83, theory requiring 15·64 per cent.). On evaporating the solution to small bulk in a vacuum and adding alcohol, a syrup is at once precipitated, which solidifies on standing, and the solution continues to deposit crystalline crusts after a time. Mannose appears to be excluded from the fact that phenylhydrazine gives no precipitate in the cold even after standing for several hours.

Fifty grams of Swedish filter-paper were treated in the manner above described, the solvent used being carbon tetrachloride, and the resulting chloromethylfurfural estimated by weighing the crystals. The residue was then extracted with water and the dextrose estimated by means of Fehling's solution. The results gave chloromethylfurfural 3·1 grams, and dextrose 1·57 grams. At first sight therefore it would

appear that the methylfurfural derivative is produced in excess. But it is found that when dextrose is treated in the same manner, a considerable portion is destroyed, leaving a black residue. A blank experiment was made with 5 grams of dextrose under exactly similar conditions, with the result that the carbon tetrachloride extract weighed only 0·01 gram, and the residual sugar 2·2 grams. If it be assumed that the dextrose resulting from the action on cellulose is destroyed to a similar extent, the calculated amount of this sugar produced in the first experiment mentioned would be 3·54 grams. This, it will be seen, is approximately the quantity required (3·86 grams) on the assumption that the chloromethylfurfural and dextrose are produced in *equal molecular proportions* (144·5 : 180).

These facts appear to be of especial interest in relation to the recent work of Skraup and König (*Ber.*, 1901, **34**, 1115), in which it is stated that the cellulose acetate obtained by the action of acetic anhydride and concentrated sulphuric acid on filter paper is an *octoacetyl biose* and that this on hydrolysis yields 'cellose,' $C_{12}H_{22}O_{11}$.

A simple explanation of the results above mentioned would be afforded if it be assumed that this 'cellose' (and its antecedent) contains both ketohexose and aldohexose residues, so that the action of hydrogen chloride could be represented by one of the following equations:
$C_{12}H_{20}O_{10} + HCl = C_6H_5O_2Cl + C_6H_{12}O_6 + 2H_2O$
$C_{12}H_{22}O_{11} + HCl = C_6H_5O_2Cl + C_6H_{12}O_6 + 3H_2O$. If the brown residue which remains after extracting the chloromethylfurfural and sugar be dried and again treated with dry hydrogen chloride as before, a further yield of both products is obtained and experiments are being made to ascertain to what extent this treatment may be repeated, and what is the nature of the final residue.

***110. "Studies in the camphane series. Part IV." By M. O. Forster.**

1-*Benzoxy-2-benzoylcamphene*, $C_8H_{14}<\begin{matrix}C\cdot CO\cdot C_6H_5\\ \|\\ C\cdot O\cdot CO\cdot C_6H_5\end{matrix}$, prepared by the action of benzoyl chloride on the sodium derivative of camphor dissolved in toluene, crystallises from alcohol in colourless, highly refractive prisms and melts at 144°; a 4 per cent. solution in chloroform has the specific rotation $[\alpha]_D = +189·7°$.

1-*Hydroxy-2-benzoylcamphene* (*enolic α-benzoylcamphor*), $C_8H_{14}<\begin{matrix}C\cdot CO\cdot C_6H_5\\ \|\\ C\cdot OH\end{matrix}$, obtained by hydrolysing the foregoing substance with alcoholic potash, crystallises from alcohol in flattened octahedra and melts at 89°; a ·2 per cent. solution in chloroform gave $[\alpha]_D = +281·1°$. It dissolves in sodium carbonate, and an alcoholic solution developes immediately an intense purple coloration with ferric

chloride; cold concentrated sulphuric acid and boiling formic acid convert it into the ketonic modification, a change which also proceeds spontaneously when the substance is dissolved in organic media, the transformation into the ketone being accelerated by addition of piperidine or by exposure to sunlight. The *sodium*, *copper*, and *ferric* derivatives are crystalline, and are freely soluble in organic liquids; the *phenylurethane* derivative melts at 117°, and the *acetyl* derivative, which crystallises from alcohol in lustrous, rectangular plates, melts at 107°.

α-*Benzoylcamphor*, $C_8H_{14}<\begin{matrix}CH\cdot CO\cdot C_6H_5\\ CO\end{matrix}$, produced on boiling a solution of the isomeride in formic acid, crystallises from alcohol in colourless, transparent prisms melting at 87—88°; a 2 per cent. solution in chloroform gave $[\alpha]_D = +125{\cdot}0°$. The alcoholic solution remains indifferent to ferric chloride at first, but a green colour is rapidly developed, and changes ultimately to bluish-violet. Fusion converts the ketone into the enolic isomeride, and the specific rotation of a solution in chloroform gradually increases until $[\alpha]_D = +216°$, the value to which the optical activity of the enol diminishes.

***111. "On the decomposition of carbon dioxide, when submitted to electric discharge at low pressures." By J. N. Collie, Ph.D.**

During some experiments that were being made on the relative resistance of carbon dioxide in a vacuum tube to the electric spark from an induction coil, it was noticed that the resistance varied considerably. At the same time, the colour of the incandescent gases at the negative electrode was seen to change. In order to ascertain what changes had taken place in the composition of the gas after sparking, the contents of the vacuum tube were pumped out and analysed. It was found that considerable decomposition had occurred into carbon monoxide and oxygen, $2CO_2 = 2CO + O_2$. A series of experiments gave the following results. When carbon dioxide at 5 mm. pressure is sparked in an ordinary vacuum tube for 10 minutes, 63 per cent. of the gas is decomposed, and when sparked for 5, 3, 2½, 1, and even ½ a minute as much as 58—60 per cent. decomposition occurs. In 15 seconds one experiment showed that 48 per cent. was decomposed, whilst in some others when the gas was sparked for 10 seconds at 10, 3, and 1 mm. pressure, 32, 55, and 65 per cent. respectively was decomposed. Most of these experiments were made with platinum electrodes. Aluminium electrodes gave a rather higher amount of decomposition, whilst with an electrodeless tube only 50 per cent. suffered decomposition after 1 minute sparking.

Another interesting observation was that if the platinum electrodes

are allowed to become red-hot, recombination at once occurs between the carbon monoxide and oxygen till the gas which remains, instead of containing the products of decomposition of 60 to 70 per cent. of the carbon dioxide, is almost pure carbon dioxide.

Under electrical strain, therefore, at low pressures, carbon dioxide is a very unstable gas, but when the products of decomposition come in contact with red-hot platinum wire recombination occurs. Carbon monoxide, even after 20 minutes' sparking, seemed almost unchanged, and gave only a faint turbidity with baryta water. When a mixture of carbon dioxide and hydrogen is sparked at reduced pressures small quantities of a gas which seems to be methane are formed, but under no conditions could formaldehyde be detected. It is probable that the methane is formed by the action of hydrogen on carbon monoxide.

***112. "Halogen derivatives of *p*-cymene from substituted nitrocamphanes." By M. O. Forster and W. Robertson.**

The oil which accompanies the conversion of 1 : 1-bromonitrocamphane into the anhydride has been identified as bromo-*p*-cymene [$CH_3 : Br : C_3H_7^{\beta} = 1 : 2 : 4$].

The *anhydride* of 1 : 1-chloronitrocamphane, prepared by dissolving that substance in cold concentrated sulphuric acid, crystallises from alcohol in colourless opaque prisms, and melts at about 230°; chloro-*p*-cymene is formed during the production of this compound. The *isomeride*, $C_{10}H_{14}ONCl$, obtained by the action of an alcoholic solution of hydrochloric acid, crystallises in transparent, six-sided plates and melts at 248°; it forms a *benzoyl* derivative which melts at 166°.

The *hydroxylamino*-derivative, $C_{10}H_{17}O_2N_2Cl$, prepared from either compound by the action of alcoholic hydroxylamine, melts at 187°; the *benzoyl* compound melts at 164°.

The *nitro*-derivative of the anhydride melting at 248° crystallises in flat prisms, which melt at 71—72°; reduction with zinc and acetic acid regenerates the anhydride.

113. "On a theory of chemical combination." By G. Martin.

Atoms are complex structures analogous to a benzene nucleus which in their ordinary state are incapable of acting on each other, but if by some cause the atomic ring is broken, the atoms become capable of acting together. In this state they are said to be "ionised." Chemical action will only take place of its own accord when the rate of variation of ether strain experienced by a molecule, produced by the approach and recedence of neighbouring molecules, is of such a rate as to coincide with an internal rate of vibration of an atom or molecule.

The atoms thus become ionised. The dissociation of gaseous molecules is controlled by two circumstances: (*a*) The gradual increase of temperature, by increasing the velocity of the atoms in the molecule, may cause it to decompose of its own accord; (*b*) if the rate of vibration of ether strain happens to coincide with the rate of vibration of the molecule, the dissociation will occur long before cause (*a*) of itself would cause decomposition.

In dissociation the atoms need not necessarily be ionised. The rapid increase of velocity of reaction with the temperature is due to the coincidence of the time rates of atomic vibration and the rate of variation of ether strain.

If two gaseous molecules, *A* and *B*, act on each other at (say) $t°$, then the same reaction will also take place at higher temperatures—$t'°$ and $t''°$—the condition being that at $t°$ the rate of variation of ether strain is approximately equal in value to the rate of vibration of the atoms of the molecule. But at $t'°$ and $t''°$ the rate of variation of ether strain is respectively double or treble the rate of atomic vibration. It may happen, however, that the products of the change are incapable of existing at these temperatures. The atoms will, however, be ionised at each of the ranges $t°$, $t'°$, and $t''°$, no matter whether any reaction takes place or not. At intermediate temperatures no reaction will take place. In certain cases we have experimental evidence of such ranges of temperature, silicon hexachloride, Si_2Cl_6, for example, is stable enough at the ordinary temperature, but above 300° its vapour begins to dissociate, and at 800° it is entirely decomposed. If, however, the temperature be raised rapidly above 1000° no decomposition of the substance occurs. The substance, therefore, is stable above 1000° and below 350°, but will not exist at intermediate temperatures.

The occurrence of these temperature ranges may be obscured by the fact that the products of the reaction may exist continuously from one range to the other.

A reaction will only proceed to completion when the rate of variation of ether strain necessary to cause the molecules to react together does not also induce the products of the change to decompose. Complete reactions occur only very seldom, as a complex molecule has so many modes of vibration that it is not difficult for it to be affected at almost any temperature.

114. "On the occurrence of paraffins in the leaf of tobacco." By T. E. Thorpe, C.B., F.R.S., and J. Holmes.

In connection with the working of the Revenue Act, which imposes a limit upon the amount of oil which may be present in manufactured tobacco, the authors have had occasion to study the nature of the

material which is extracted from tobacco by 'petroleum-ether.' In the extract thus obtained, they have discovered the presence of two paraffins, *hentriacontane*, $C_{31}H_{64}$, melting at 67·8—68·5°, and *heptacosane*, $C_{27}H_{56}$, melting at 59·3—59·8°, which are present in the leaf in about equal amounts to the extent, in the aggregate, of rather more than 1 part per 1000.

In Kentucky and Virginia leaf, the mixed hydrocarbons, in three separate preparations, had the following melting points: western leaf, 63·0—63·8°; "wrappers," 63·5—64·0°; "fillers," 63·7—65·0°. The authors are of opinion that the snow-white substance of satiny lustre extracted from Kentucky tobacco by Kissling (*Ber.*, 1883, **16**, 2432), which he found to melt at 63·0° and which he regarded as probably an impure mellissyl mellisate, and the substance of similar appearance found by him among the constituents of tobacco-smoke, melting at 64·5°, but which he regarded as a hydrocarbon, are in reality the same products, and identical with the mixture of the two paraffins, the heptacosane, $C_{27}H_{56}$, and hentriacontane, $C_{31}H_{64}$, of Krafft, which the authors have found to be present in all the American tobaccos examined by them.

115. "Two new substances in lemon oil." By H. E. Burgess.

If 3 or 4 litres of the terpenes obtained during the distillation of the lemon oil are well shaken with a cold solution of sodium metabisulphite, a small quantity of a crystalline compound is formed which can be separated and washed with alcohol and ether. This on being decomposed in the usual way gives an aldehyde of which the constants are very different from those of citral:—boiling point, 80—85° at 15 mm.; optical rotation, +0°·30′; refractive index, 1·4314 at 20°.

It has an odour resembling cocoanut oil. On shaking the aldehyde with hydrogen peroxide and caustic soda solution it is at once polymerised into a solid form which can be recrystallised from alcohol.

It forms an oxime melting at 35°, and on oxidation with potassium permanganate it gives an oily acid; from the ammonium salt the silver, copper, and magnesium salts have been prepared and analysed.

Apparently the same aldehyde exists in orange oil, but was not found in the terpenes as in the case of lemon oil.

A crystalline substance was obtained by shaking together one litre each of acetone and lemon oil and then adding about 200 c.c. of water, when it separates into two layers; the lower portion was separated and allowed to stand for 24 hours, when small crystals were formed in the globules of oil floating on the surface; these were filtered off and recrystallised from alcohol and ether.

Several such separations may be made from each quantity of oil,

but the total yield from one litre was extremely small. The crystals so obtained melted at 145°. They are sparingly soluble in alcohol, the solution having a marked blue fluorescence.

Several combustions have been made of the recrystallised substance which forms a crystalline dibromide and is oxidised to oxalic acid and carbonic acid.

116. "Preparation and properties of 2 : 6-diketo-4-isopropylhexamethylene (2 : 6-dihydroxy-4-isopropyldihydroresorcinol)." By A. W. Crossley.

Ethyl 2 : 6-*diketo*-4-*isopropylhexamethylene*-3-*carboxylate*, obtained by the condensation of *iso*butylideneacetone and ethyl malonate, separates from a mixture of benzene and light petroleum in small needles melting at 101°. When boiled with sodium carbonate or potassium hydroxide solution it yields:

2 : 6-*Diketo*-4-*isopropylhexamethylene*, $C_3H_7C\begin{matrix}CH_2\cdot CO\\ H\\ CH_2\cdot CO\end{matrix}CH_2$, which crystallises from dilute alcohol, with $1H_2O$, in well formed needles melting at 67·5°. Its constitution is proved by its method of formation and because on oxidation with sodium hypobromite it yields *β-iso*propylglutaric acid. The *silver* salt is an insoluble white precipitate and the *dioxime* separates from dilute methyl alcohol in clusters of stumpy needles melting somewhat indefinitely about 145°.

When hydrolysed with barium hydroxide diketo*iso*propylhexamethylene is converted quantitatively into *β-isopropyl-γ-acetylbutyric acid*, $C_3H_7C\begin{matrix}CH_2\cdot CO_2H\\ H\\ CH_2\cdot CO\cdot CH_3\end{matrix}$, which is an almost colourless oil boiling at 195° (39 mm.).

117. "Action of bromine on the three toluene azophenols." By J. T. Hewitt and J. N. Tervet.

In continuation of the work of one of the authors and his pupils on the substitution of oxyazo-compounds, the bromination of the three tolueneazophenols has now been studied. In glacial acetic acid solution, sodium acetate being present, toluene azodibromophenols result in all these cases, the reactions being quite analogous to those observed with phenol itself. Metatolueneazophenol brominates smoothly only if the solution in acetic acid is well cooled whilst the bromine is added.

The following substances have been prepared: *o-tolueneazodibromophenol*, m. p. 121°; *ethyl ether*, m. p. 95°; *acetyl* derivative, m. p. 153°; *benzoyl* derivative, m. p. 169°; *m-tolueneazodibromophenol*, m.p. 129°; *ethyl ether*, m. p. 88°; *acetyl* derivative, m. p. 118°; *benzoyl*

derivative, m. p. 141°; *p-tolueneazophenol*, m. p. 137°; *ethyl ether*, m. p. 95°; *acetyl* derivative, m. p. 148°; *benzoyl* derivative, m. p. 114°.

118. "Reduction of αγ-dibenzoylpropane and dibenzoyldiphenylbutadiene." By F. R. Japp, F.R.S., and A. C. Michie, B.Sc.

By the action of sodium on an ethereal solution of αγ-dibenzoylpropane, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$, floating on water, J. Wislicenus and Kuhn (*Annalen*, 1898, **302**, 221) obtained a "pale yellow oil" which they regard as the cyclic pinacone, 1 : 2-*diphenyl*-1 : 2 *dihydroxy*cyclo*pentane*, $\begin{matrix} C_6H_5{\cdot}C(OH){\cdot}CH_2 \\ C_6H_5{\cdot}C(OH){\cdot}CH_2 \end{matrix}\!\!>\!CH_2$. The present authors show that this oil is, in reality, a very complex mixture. The pinacone, which when pure forms colourless needles showing oblique extinction and melting at 103—104·5°, is contained in it to the extent of about 50 per cent. From glacial acetic acid the pinacone is deposited in large, sparingly soluble crystals of the formula $C_{17}H_{18}O_2,C_2H_4O_2$, in which form it may be separated from the other substances present. A quantitative yield of it may be obtained by the reduction of dibenzoylpropane in hot aqueous alcoholic solution with aluminium amalgam. Oxidised with chromium trioxide, it regenerates dibenzoylpropane. In addition to the pinacone, the "pale yellow oil" contains, along with other substances, a small quantity of *αε-diphenyl-αε-dihydroxypentane*, $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_5$, lustrous, slender, six-sided prisms showing straight extinction and melting at 84—88° to a turbid liquid which clears at 92°. A better although still unsatisfactory yield of the latter substance is obtained by reducing dibenzoylpropane in boiling alcoholic solution with sodium.

By reducing the "pale yellow oil" with hydriodic acid, Wislicenus and Kuhn prepared a hydrocarbon melting at 108° to which they assign the constitution of a 1 : 2-*diphenylcyclopentane*. The authors find that this supposed 1 : 2-diphenyl*cyclo*pentane is a highly polymerised substance which does not boil even at 340° under a pressure of 12 mm., whereas the known 1 : 2-diphenyl*cyclo*pentane (m. p. 47°) obtained from anhydracetonebenzil (Japp and Burton, *Trans.*, 1887, **51**, 423; Japp and Lander, *ibid.*, 1897, **71**, 128 and 131), the existence of which has been overlooked by Wislicenus and Kuhn, boils at 189° under a pressure of 12 mm. The authors give a further proof of the constitution of the latter 1 : 2-diphenyl*cyclo*pentane by oxidising it to αγ-dibenzoylpropane.

J. Wislicenus and Lehmann (*Annalen*, 1898, **302**, 214), by reducing dibenzoyldiphenylbutadiene with hydriodic acid, obtain, along with other products, a substance melting at 92—94° to which they assign the formula $C_{20}H_{14}O$. The authors find that this compound has in

reality the formula $C_{22}H_{16}O$, and is **2 : 3 : 5-*triphenylfurfuran*** (Japp and Klingemann, *Trans.*, 1890, **57**, 663), and that ***acetophenone*** is simultaneously formed, the reaction taking place as follows:

(1) $\begin{matrix}C_6H_5\cdot C{:}CH\cdot CO\cdot C_6H_5\\ C_6H_5\cdot C{:}CH\cdot CO\cdot C_6H_5\end{matrix} + H_2O =$

$\begin{matrix}C_6H_5\cdot C{:}CH\cdot CO\cdot C_6H_5\\ C_6H_5\cdot CO\end{matrix} + C_6H_5\cdot CO\cdot CH_3;$

$\alpha\beta$-Dibenzoylphenylethylene.

(2) $\begin{matrix}C_6H_5\cdot C{=}CH\\ C_6H_5\cdot CO \quad CO\cdot C_6H_5\end{matrix} + 2H = \begin{matrix}C_6H_5\cdot C{-}CH\\ C_6H_5\cdot C \quad C\cdot C_6H_5\\ \quad\quad O\end{matrix} + H_2O.$

For the sake of simplicity, the symmetrical formula for dibenzoyldiphenylbutadiene has been employed; but the validity of the explanation is quite independent of this.

The various papers on the condensations of benzil with ketones published by one of the authors, conjointly with others, have, with one exception, been overlooked by J. Wislicenus and his pupils, and the errors into which they have fallen are in part attributable to this cause.

119. "Homologues of anhydracetonebenzil." By F. R. Japp, F.R.S., and A. N. Meldrum, B.Sc.

The authors find that under the influence of potassium hydroxide benzil condenses with homologues of acetone of the general formulæ $CH_2R\cdot CO\cdot CH_3$, $CHR_2\cdot CO\cdot CH_3$, $CH_2R\cdot CO\cdot CH_2R$, and $CHR_2\cdot CO\cdot CH_2R$, to form homologues of anhydracetonebenzil (*diphenylcyclopentenolone*), $\begin{matrix}C_6H_5\cdot C{=}{}^{\alpha}CH\\ C_6H_5\cdot C(OH)\cdot CH_2{}^{\beta}\end{matrix}>CO$. In naming these compounds the CH group in the pentacarbon ring is distinguished as the α- and the CH_2 group as the β-position. Thus benzil and methyl ethyl ketone yield ***α-methylanhydracetonebenzil***, $\begin{matrix}C_6H_5\cdot C{=}C(CH_3)\\ C_6H_5\cdot C(OH)\cdot CH_2\end{matrix}>CO$ (large, flat, lozenge-shaped crystals melting at 118°), and ***β-methylanhydracetonebenzil***, $\begin{matrix}C_6H_5\cdot C{=}CH\\ C_6H_5\cdot C(OH)\cdot CH(CH_3)\end{matrix}>CO$ (prisms, melting at 180°)—the latter already prepared by Japp and Burton (*Trans.*, 1887, **51**, 431)—whilst at the same time an open-chain compound, ***desylene-methyl ethyl ketone***, $\begin{matrix}C_6H_5\cdot C{:}CH\cdot CO\cdot C_2H_5\\ C_6H_5\cdot CO\end{matrix}$ (m. p. 157°), is formed. The latter substance is more readily obtained by boiling β-methylanhydracetonebenzil with

glacial acetic acid, and, on the other hand, is reconverted into the β-compound by heating at 300—320°.

The authors show that the sparingly soluble monalkyl homologues of anhydracetonebenzil prepared by Japp and Burton by heating a mixture of benzil and homologues of acetone with aqueous potassium hydroxide, belong to the β-series, and that readily soluble α-isomerides, overlooked by these authors, are formed in small quantity at the same time. By using cold alcoholic potassium hydroxide as a condensing agent, the α-compounds may be obtained in larger quantity. All the α-compounds are distinguished by forming benzylidene derivatives when treated with benzaldehyde and alcoholic potassium hydroxide.

With benzil and alcoholic potassium hydroxide, α-methylanhydracetonebenzil yields *α-methylanhydracetonedibenzil*, $C_{32}H_{26}O_4$ (dimorphous: silky needles, m. p. 185°; and warty crystals, m. p. 194°), which is obtained in the form of a complex potassium salt, $C_{32}H_{23}O_4K,C_{32}H_{26}O_4,4C_2H_5{\cdot}OH$. The sodium salt may be obtained directly from benzil and methyl ethyl ketone by condensation with alcoholic sodium ethoxide. α-Methylanhydracetonedibenzil is ethylated by boiling it with alcohol and sulphuric acid, yielding the compound $C_{32}H_{25}(OC_2H_5)O_3$ (short needles, melting at 250°).

Both α- and β-methylanhydracetonebenzil are transformed, by brief boiling with hydriodic acid, into the same *methyldiphenylcyclopentenone*, $C_6H_5{\cdot}C{\cdot}CH(CH_3)$ / $C_6H_5{\cdot}C$ ——— CH_2 >CO (faint yellow, oblique, flat prisms or plates, m. p. 77—78°), which yields a *phenylhydrazone*, $C_{21}H_{22}N_2$, melting at 145—152°. By boiling α-methylanhydracetonebenzil for 5 hours with hydriodic acid and red phosphorus, the methyldiphenylcyclopentenone, which is first formed, is in its turn reduced to *1-methyl-2:3-diphenylcyclopentane*, $C_6H_5{\cdot}CH{\cdot}CH(CH_3)$ / $C_6H_5{\cdot}CH$ ——— CH_2 >CH_2 (m. p. 62—63°), already obtained by Japp and Murray (*Trans.*, 1897, 71, 153) by the reduction of α-anhydrobenzillævulic acid, the carboxyl group being eliminated in the latter case.

By boiling with slightly diluted sulphuric acid, or with glacial acetic acid, α-methylanhydracetonebenzil yields a dehydration product, $C_{26}H_{28}O_2$ (m. p. 230°, with evolution of gas). β-Methylanhydracetonebenzil, when heated with formic acid, gives the same product.

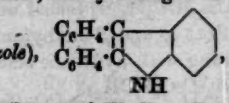
In addition to the foregoing, the following compounds have been prepared: *Benzylidene-α-methylanhydracetonebenzil*, m. p. 225°; *α-desylene-ethyl ethyl ketone*, $C_6H_5{\cdot}C{:}C(CH_3){\cdot}CO{\cdot}C_2H_5$ / $C_6H_5{\cdot}CO$, m. p. 128°, converted, on heating, into *αβ-dimethylanhydracetonebenzil*, m. p. 150°; *ββ-dimethylanhydracetonebenzil*, m. p. 181°; *α-ethylanhydracetonebenzil*, m. p. 114°, and its *benzylidene* derivative, m. p. 178°

aββ-trimethylanhydracetonebenzil, m. p. 131°; *a-propylanhydracetonebenzil*, m. p. 89°, and its *benzylidene* derivative, m. p. 166°; *β-propylanhydracetonebenzil*, m. p. 152°; *aβ-diethylanhydracetonebenzil*, m. p. 113—114°; *a-amylanhydracetonebenzil*, m. p. 57°, and its *benzylidene* derivative, m. p. 156°.

All *β*-monalkylanhydracetonebenzils corresponding with these *a*-compounds, but not included in the foregoing list, have been already described by Japp and Burton (*loc. cit.*).

The oxidation products of the various methylanhydracetonebenzils are at present under investigation.

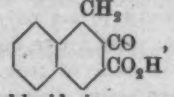
120. "Formation of carbazoles: a preliminary note." By F. R. Japp, F.R.S., and W. Maitland, B.Sc.

The fact that *β*-phenanthrol (*phenanthrone*), $\begin{matrix}C_6H_4\cdot CH\\ C_6H_4\cdot C\cdot OH\end{matrix}$, interacts, apparently in the keto-form, $\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CO\end{matrix}$, with phenylhydrazine, eliminating simultaneously water and ammonia, and yielding 2′:3′-diphenyleneindole (*phenyl-β-phenanthrylcarbazole*),  , as in E. Fischer's synthesis of indoles (compare Japp and Findlay, *Trans.*, 1897, 71, 1117), led the authors to try whether *β*-naphthol, which *β*-phenanthrol in many respects resembles, would behave in an analogous manner. On heating *β*-naphthol with excess of phenylhydrazine there was no reaction, but on adding to the mixture some phenylhydrazine hydrochloride and continuing the heating, water and ammonia were evolved, and a fair yield of a *phenyl-β-naphthylcarbazole*, $\begin{matrix}C_6H_4\\ C_{10}H_6\end{matrix}>NH$ (needles melting at 134—135°), was obtained. The reaction does not take place when *β*-naphthol is heated with phenylhydrazine hydrochloride alone.

The following derivatives of this carbazole were prepared and analysed: *nitroso*-derivative, yellow flat needles, m. p. 144—145° (with decomposition); *acetyl* derivative, small pearly laminæ, m. p. 149°; *benzoyl* derivative, slender needles, m. p. 189·5°.

Two phenyl-*β*-naphthylcarbazoles—the number predicted by theory—are already known: one melting at 330°, isolated by Graebe and Knecht from coal-tar and afterwards synthesised by them by passing the vapour of phenyl-*β*-naphthylamine through a red-hot tube (*Annalen*, 1880, 202, 1); and a second obtained by Schöpff (*Ber.*, 1896, 29, 269) by elimination of carbon dioxide from phenyl-*β*-naphthylcarbazolecarboxylic

acid, and asserted by him to melt at 120°. The melting points of the derivatives are given by Schöpff as follows: *nitroso*-derivative, 132°; *acetyl* derivative, 142°; *benzoyl* derivative, 170°. With the exception, however, of these very considerable differences in the melting points, the descriptions given by Schöpff of his compounds would apply to those prepared by the authors; moreover, various colour reactions which he mentions are the same in both cases. The authors, therefore, prepared Schöpff's phenyl-β-naphthylcarbazole by his method, and found that it melted at 134—135° (instead of at 120°, as stated by him) and was absolutely indistinguishable from their compound. As the yield by Schöpff's method is very poor, they did not trouble to prepare the derivatives over again from substances obtained in this way; but they have no doubt that similar errors in the determination of the melting points have been committed by the German investigator in the case of these also.

Schöpff obtained his phenyl-β-naphthylcarbazolecarboxylic acid by heating 3-hydroxy-β-naphthoic acid (m. p. 216°) with phenylhydrazine, a reaction which would correspond with that described by the authors, except that this so-called hydroxynaphthoic acid is the keto-form dihydro-2-keto-3-naphthoic acid,  , and that the addition of phenylhydrazine hydrochloride is unnecessary.

α-Naphthol, when heated with the mixture of phenylhydrazine and its hydrochloride, yielded *phenyl-α-naphthylcarbazole* (m. p. 225·5°), already obtained by Kym (*Ber.*, 1890, **23**, 2465) by desulphurising thiophenyl-α-naphthylamine with finely divided copper. The present reaction does not take place so readily as with β-naphthol, and the yield is small.

The authors are engaged in extending this reaction to other phenols and to other arylhydrazines in presence of their hydrochlorides.

121. **"Metal-ammonia compounds in aqueous solution. Part III. Solutions of salts of the alkaline earth metals." By H. M. Dawson and J. McCrae.**

The distribution of ammonia between solutions of salts of the alkaline earth metals and chloroform has been determined at 20°, and the results obtained indicate that the calcium ions form complex ammonia ions to a slight extent in solution, whilst the strontium ion possesses the power of fixing ammonia in a less degree, and the barium ion has the lowest power.

122. **"Metal-ammonia compounds in aqueous solution. Part IV. The influence of temperature on the dissociation of cupri-ammonia sulphate." By H. M. Dawson and J. McCrae.**

The distribution of ammonia between water and chloroform and between aqueous copper sulphate and chloroform has been determined at 10° and 30°. The results indicate that the copper sulphate fixes more ammonia at the lower than at the higher temperature; but no exact quantitative statement can be made as to the influence of temperature on the dissociation of the compound $Cu4NH_3 \cdot SO_4$, since within the limits of temperature at which the experiments were made this influence is very small.

The same relationship between ammonia concentration and distribution coefficient has been found at 10° and 30° as that previously observed at 20° (*Trans.*, 1901, 79, 496).

123. **"On the combined action of diastase and yeast on starch-granules." By G. H. Morris, Ph.D.**

When yeast is allowed to act on a solution of starch-conversion products in the presence of active diastase, the quantity of matter fermented is greatly in excess of that which can be fermented by the yeast alone; and when active diastase and yeast are allowed to act conjointly on the so-called stable-dextrin, which under ordinary conditions is neither degradable by diastase nor fermentable by yeast it is entirely fermented.

It is now shown that a similar action takes place when certain ungelatinised starch-granules are submitted to the joint action of malt-extract and yeast, the quantity of starch decomposed by the joint action being about three times that dissolved by malt-extract alone. The increased action in the presence of yeast is not due to the removal of the soluble product, maltose, from the field of action, and the consequent greater activity of the diastase. No increased diastatic action takes place in the presence of yeast if the fermentative power of the latter is checked by chloroform, neither does any increase of action take place when the malt-extract is submitted to fermentation, and the yeast-cells removed, before the addition of the starch-granules.

Precipitated diastase behaves in the same way as cold water malt-extract, but to a lesser extent.

The combined action of diastase and yeast only occurs with those starches which are attacked in the ungelatinised form by diastase, such as barley or malt starch. The granules of potato starch are not acted on by diastase even in the presence of yeast.

124. "A calibrating mercury pipette." By C. A. Bell, M.B.

The little device figured in the diagram will be found very useful in calibrations of all kinds. It is easily constructed on any scale; the volume of mercury delivered by it is for all practical purposes constant, and the time saved by its use is considerable.

The mercury reservoir, *A*, is made from a piece of soft German or soft Jena tubing, of moderate wall thickness and free from internal flaws. At the lower end it is drawn out to a narrow tube terminating in an orifice about 0·4 mm. in diameter. The edge of this orifice may be slightly fused, but not so as to invert it. At its upper end, *A* is drawn out to a very fine capillary tube, which should be of such diameter at its narrowest section that a pressure of *at least* 15 cm. of mercury is required to drive the metal through it. A short tube of such narrow bore is not easily prepared in an ordinary blow-pipe or Bunsen flame; the final drawing may, however, be easily effected in the outer mantle of a candle-flame, as in preparing a Lippmann's capillary electrometer. The little tube so formed should be cut at such a point that the diameter of the portion left on *A* (from 1 to 1·5 cm. in length) diminishes continuously from *A* to the end. A constantly increasing pressure is then required to drive mercury nearer and nearer to the orifice.

The reservoir *A* thus prepared is cemented, as shown, air-tight into a somewhat wider tube, *B*, which is drawn out at its upper end so that an india-rubber tube may be attached to it. The cement used may be sealing-wax; but if *B* is just wide enough to receive *A*, a much neater joint may be made with fused silver chloride. A little of the chloride is melted in a porcelain crucible and the well heated end of *B* dipped into it repeatedly until a sufficient quantity of the chloride has been collected. That which adheres to the inner surface of *B* is removed with a penknife; the previously warmed end of *A* is then passed into *B*, and the two tubes heated together high above a Bunsen flame, to avoid reduction of the silver, until the chloride melts. When prepared in this way, the pipette may be heated and dried by a current of air, if necessary, without disconnecting *A* and *B*.

To use the pipette, an india-rubber tube of some length is slipped over the narrow end of *B*, and secured air-tight by a few turns of soft copper wire, the ends of the wire being left loose. The point of the pipette is then plunged well below the surface of mercury contained in a bottle or basin, and suction applied until the metal rises to within a couple of millimetres of the capillary orifice. If the capillary tube has been properly formed, it can, without the slightest difficulty,

be brought to any desired level which may be marked on the outside of *B*; but generally it is sufficient to bring it within a short distance of the orifice. A rather coarse capillary measured by a microscope micrometer was found to have, at the orifice, a diameter of 0·008 cm. The capacity of a tube of this diameter is only 0·00005 c.c. per centimetre of length, so that a variation in the level of a millimetre either way is of small importance.

The filling having been accomplished, the rubber tube is pinched; the pipette may then be lifted and carried about without the loss of a particle of mercury, so long as it is held in a nearly vertical position. Inclining it, however, by increasing the effective pressure on the capillary, may cause mercury to pass from *A* to *B*. This is much less likely to happen when in the process of filling the mercury has not been drawn right up to the orifice; the pressure may then increase or diminish considerably without causing the escape of mercury from either end of *A*.

In discharging the pipette, the pressure of the fingers on the rubber tube having been released, the mercury is allowed to trickle gently down the side of the tube or vessel to be calibrated. Usually a short thread of metal remains in the lower prolongation of *A*; this is best removed by pinching the rubber tube near its open end with the fingers of the hand holding the pipette, and compressing it about its centre with the other hand. It is not advisable to blow into *B*, as in the course of a calibration moisture from the breath may find its way into *A*, causing the formation of air bubbles within it.

As air bubbles never form in *A* when the mercury entering it is dry and free from surface impurities, any sensible variation in the volume delivered at constant temperature can be due only to variations in the point at which disruption occurs in the mercury when the pipette is raised. These, however, are exceedingly small. In a series of tests with a pipette holding about 17 grams of mercury, and having an outflow orifice 0·05 cm. in diameter, the weight of mercury delivered was constant within 0·0005 gram, or in volume 0·00004 c.c. By making the outflow orifice very small, still greater constancy can be secured; but the time occupied in charging and emptying is then greatly increased. In conducting a test of this kind, of course, the temperature of the mercury must be carefully observed. Mercury contained in a bottle or jar can never be assumed to be at room temperature, and when poured into a basin its temperature may alter rapidly from a variety of causes.

Sometimes a small globule of metal sticks very persistently in the lower constricted part of *A*. Such a globule can usually be rinsed out by sucking back a little of the metal already delivered, especially if the part of the tube containing it has been previously warmed.

The advantages of this pipette over Bunsen's well-known calibrating device are obvious. The quantity of mercury required for any calibration is a minimum; the metal need never be touched by the fingers; and as surface impurities are excluded by the pipette, which acts as a filter, the mercury delivered by it is always bright and clean, and lies in perfect contact with the wall of the receiving vessel.

125. "α-Amido-β-methylhydrindene." By F. S. Kipping and G. Clarke.

The authors have prepared α-amido-β-methylhydrindene, $C_6H_4<\begin{matrix}CH_2\cdot CHMe\\CH(NH_2)\end{matrix}>$, in order to study the salts obtained by combining it with various optically active acids, and thus perhaps to elucidate the curious behaviour of its lower homologue hydrindamine (Kipping, *Trans.*, 1900, **77**, 861; and Kipping and Hall, *Trans.*, 1901, **79**, 442).

β-Methylhydrindone, $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CH\cdot Me$, is easily obtained by the action of aluminium chloride on α-methylhydrocinnamic chloride, ring formation taking place with the elimination of hydrogen chloride (compare Kipping, *Trans.*, 1894, **65**, 680; Kipping and Hill, *Trans.*, 1899, **75**, 144; and Kipping and Hunter, *Trans.*, 1901, **79**, 604).

This method gives much better results than the treatment of the acid with concentrated sulphuric acid (von Miller and Rhode, *Ber.*, 1890, **23**, 1888), the yield being from 70 to 80 per cent. of the theoretical.

β-Methyl-α-hydrindoxime crystallises in well-defined octahedra melting at about 103°. The base, of which the formula is given above, is obtained by reducing the oxime with sodium amalgam in dilute acetic acid solution. It resembles hydrindamine in general properties.

Since α-amido-β-methylhydrindene contains two asymmetric carbon groups, it should consist of four optically different forms, and when combined with optically inactive acids it might be expected to give rise to two series of salts.

As a matter of fact, on fractionally crystallising the *hydrochloride* of the original base from water, it is resolved into a sparingly soluble salt which forms long, silky needles decomposing at about 252°, and a readily soluble salt which is obtained in small, ill-defined nodular masses decomposing at about 225°.

The two hydrochlorides are probably the salts of the two externally compensated ($\begin{matrix}+&-\\+&-\end{matrix}$ and $\begin{matrix}+&-\\-&+\end{matrix}$) bases, but the more readily soluble one may not be quite free from its isomeride. The sparingly soluble salt gives a *platinichloride*, $(C_{10}H_{13}N)_2,H_2PtCl_6+2H_2O$, which crystallises

from water in lustrous, yellow plates decomposing at about 192°, whilst the readily soluble isomeride gives a *platinichloride*, $(C_{10}H_{15}N)_2,H_2PtCl_6$, which is anhydrous, and decomposes at about 202°.

The *benzoyl* derivative prepared from the sparingly soluble hydrochloride crystallises in silky needles melting at 169°, whereas the corresponding compound, obtained from the readily soluble hydrochloride, melts at about 138°.

The *sulphate* of the original base crystallises in large transparent prisms, and does not seem to be resolved into different products when fractionally crystallised from water.

The investigation of these bases is being continued.

126. "Stereoisomeric α- and α′-sulphonic derivatives of camphor." By H. E. Armstrong and T. M. Lowry.

The authors have further examined Reychler's camphorsulphonic acid, prepared by sulphonating camphor by means of a mixture of sulphuric acid and acetic anhydride; they have also prepared corresponding acids from chloro- and bromo-camphor which are reducible to Reychler's acid. They confirm Reychler's observation that two camphorsulphonamides are formed by the action of ammonia on the sulphochloride, and show that this is not due to any want of homogeneity in the latter, but to the occurrence of isomeric change during the interaction.

Reychler's camphorsulphonic acid is probably an α-acid, the sulpho-group occupying the same position as the bromine atom in α-bromocamphor. When the sulphochloride or sulphobromide is acted on with dilute ammonia the action proceeds normally, only the α-sulphonamide, m. p. 223°, being produced; the isomeric α′-sulphonamide, m. p. 132°, is formed when strong ammonia is used and the action is allowed to proceed violently; it is a labile substance, and is readily converted into the stable α-sulphonamide by the action of bromine or of mineral acids.

Camphor-α-sulphobromide, m. p. 93°, $[\alpha]_D$ +26°. *Camphor-α-sulpho-p-bromoanilide*, m. p. 165°, $[\alpha]_D$ +56°. *Camphorsulphopiperidide*, m. p. 140°, $[\alpha]_D$ +32·2°, is the chief product of the action of piperidine on the sulphochloride, but a more soluble *piperidide*, m. p. 55°, $[\alpha]_D$ +33·6°, is also produced.

α-Bromocamphor-α′-sulphonic acid is readily isolated in the form of the *calcium* salt, $(C_{10}H_{15}SO_4)_2Ca + 6H_2O$; this crystallises from hot water in pearly scales. The *sulphochloride*, m. p. 65°, $[\alpha]_D$ +104°, yields a single *sulphonamide*, m. p. 156°, $[\alpha]_D$ +106°, which is reduced by zinc dust and acetic acid to camphor-α′-sulphonamide. The *sulphoanilide*, m. p. 106°, $[\alpha]_D$ +177°, is reduced to camphor-α-sulphoanilide. The

sulphopiperidide, m. p. 123°, $[\alpha]_D$ +111°, is reduced to the camphor-sulphopiperidide melting at 140°.

α-Chlorocamphor-α'-sulphochloride has m. p. 60°, $[\alpha]_D$ +81°. The *sulphonamide*, m. p. 141°, $[\alpha]_D$ +83°, is reduced to camphor-α-sulphonamide.

When α-bromocamphor-α'-sulphonamide is boiled with acetic anhydride it is converted into an *anhydride*, $C_{10}H_{14}BrSO_2N$, m. p. 186°, $[\alpha]_D$ +98°, to which the formula $C_8H_{14}\begin{cases}CBr\cdot SO_2\\ |\quad\quad |\\ C=\!=N\end{cases}$, may perhaps be assigned; it is reduced by zinc dust and acetic acid to camphor-α-sulphonamide. By the action of bromine on camphor-sulphonamide or of bromhydric acid on α-bromocamphor-α'-sulphonamide, the *stereoisomeric anhydride* of α'-bromocamphor-α-sulphonamide, m. p. 166°, $[\alpha]_D$ +41°, is also produced. By the further action of bromine these are converted into the *anhydride*, $C_{10}H_{13}Br_2SO_2N$, of a *dibromocamphorsulphonamide*, m. p. 195°, $[\alpha]_D$ −7°, which on reduction yields camphor-α-sulphonamide.

The *anhydride* of *α-chlorocamphor-α'-sulphonamide* m. p. 167°, $[\alpha]_D$ +60°, yields camphor-α-sulphonamide on reduction. An *anhydride*, $C_{10}H_{13}Cl_2SO_2N$, of a *dichlorocamphorsulphonamide* may be prepared by the action of chlorine on camphorsulphonamide, chlorocamphorsulphonamide, or its anhydride; m. p. 172°, $[\alpha]_D$ +4°, on reduction this yields camphor-α-sulphonamide.

127. "Displacement of alkyls from phenols by nitration. I. Thymol." By A. T. Larter.

Maldotti, in a recent note (*Gazzetta*, 1900, 30, ii, 365), states that trinitrothymol is formed on nitrating dinitrothymol; he was unable to analyse the product, and bases his statement solely on molecular weight determinations made by the cryoscopic method. This conclusion is in opposition to the result arrived at by Armstrong and Rennie (*Chem. News*, 1883, 47, 115), who found that the so called trinitrothymol was in reality trinitrometacresol.

The author has repeated the experiments at Dr. Armstrong's request, and his results confirm the conclusion arrived at by Armstrong and Rennie.

The melting point of the product from thymol is the same as that of trinitrometacresol, and is unaffected when the substance is mixed with the trinitro-compound prepared from metacresol. On methylation, the product affords an ether identical with that prepared from trinitrometacresol, the two substances melting at 91°, whether singly or in admixture, and giving the same trinitrometatoluidine (m. p. 136°) when subjected to the action of ammonia.

When dinitrothymol ethyl ether is subjected to nitration, it is converted into trinitrometacresol ethyl ether—an observation of importance as proving that the displacement of the alkyl does not involve the formation at an intermediate stage of a keto-compound.

128. "Taka-diastase and reversed ferment action." By A. C. Hill.

The hydrolysis of dilute starch solutions by taka-diastase ends in an almost complete transformation to glucose, as shown by the combined polarimetric and copper reduction methods of estimation; no dextrin which resists further hydrolysis is formed, and there is sufficient maltase in commercial taka-diastase to convert all the maltose to glucose.

A solution containing 35 per cent. of glucose and 6 per cent. of maltose hydrate, that is, 41 per cent. of total sugar, on treatment by taka-diastase containing maltase, was further hydrolysed until the measurements indicated nearly 39 per cent. of glucose and about 2 per cent. of maltose hydrate. A 60 per cent. solution of glucose, however, similarly treated, showed a reversed ferment action until its optical and reducing properties corresponded with those of a solution containing 58 per cent. of glucose and 2 per cent. of maltose hydrate. On diluting the solution without boiling, hydrolysis again took place. The difference in equilibrium point in this case from that found by the author when acting on concentrated glucose solutions with yeast extract (*Trans.*, 1898, 73, 634) (in the latter case the measurements at equilibrium corresponded to a mixture of 34 per cent. of glucose and 6 per cent. of maltose hydrate) is probably to be explained by the presence in the yeast extract of enzymes other than maltase and diastase, whereby other polysaccharides are formed either from glucose or maltose, such ferment actions being quite distinct from a possible formation of higher polysaccharides from maltose, which may occur also in the case of taka-diastase.

LIBRARY.

The Library will be closed for stock-taking during the first fortnight of August. Fellows are particularly requested to return all Library books in their possession not later than July 27th.

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PROCEEDINGS

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The following are abstracts of papers received during the vacation and published, or passed for publication, in the *Transactions*:

129. Additional notes on dinitro-orthoanisidine. A chemical reaction in which one of the products continues the same reaction. By R. Meldola and J. V. Eyre.

The authors give further evidence in support of the constitutional formula assigned to the dinitroanisidine already described (*Proc.*, 1901, **17**, 131). The 3 : 4 : 6-triaminoanisole and the corresponding 3 : 4-diamino-6-acetaminoanisole both form azines on condensation with benzil, which are described. The view put forward (*loc. cit.*), that the eliminated nitro-group comes out in the form of nitrous acid, is confirmed by quantitative determinations of the amount of diazo-oxide formed from known weights of dinitroanisidine in acetic acid solution with accurately titrated solutions of nitrite. The latter was added to the extent of one-fourth of the theoretical quantity required on the assumption that one molecule of dinitroanisidine requires one molecule of nitrite. In all cases the diazo-oxide produced, as determined by the quantity of azo-β-naphthol compound formed, was far in excess of that capable of being produced by the nitrite added, thus proving that the nitro-group eliminated by the nitrous acid continues the process of diazotisation.

130. "Ethyl sec-octyl tartrate and its dibenzoyl and diacetyl derivatives." By J. McCrae.

Diethyl tartrate and octyl alcohol when saturated in the cold with hydrochloric acid give ethyl octyl tartrate, which is purified by distillation and washing with water. By the action of excess of acid chloride on this mixed ester, the dibenzoyl and diacetyl derivatives have been prepared. The optical rotation of these compounds has been determined, and the author finds that the molecular rotations are similar to the constants for the corresponding diethyl tartrates. This is a confirmation of the rule suggested by Guye, namely, that when substitution is effected at a point sufficiently far removed from the asymmetric carbon atom, only a slight change in the rotation is produced.

131. "The esterification of 3-nitrophthalic acid." By A. McKenzie.

The esterification of 3-nitrophthalic acid does not proceed normally in accordance with V. Meyer's rule. The author has studied the action of amyl and methyl alcohols on 3-nitrophthalic acid and its anhydride, and shows that the isomeric α- and β-acid esters are formed on esterification, as well as the neutral ester in certain cases.

The compounds 2-*iso*amyl-3-nitrophthalic acid and *d*-2-amyl-3-nitrophthalic acid are also described.

132. "Derivatives of 3-nitrotolyl-4-hydrazine." By F. G. Pope and J. M. Hird.

The *hydrochloride* was prepared by Meyer and Lecco's method, and forms orange-red plates or needles, m. p. 190—191° with decomposition. The free base forms red tufts of needles, m. p. 110°. The *pyruvic acid hydrazone* forms yellow needles, m. p. 203° with decomposition. The *ethyl ester* of the pyruvic hydrazone is obtained as small, yellow needles, m. p. 140°. The *semicarbazide* forms small, yellow needles m. p. 201°, and gives a deep violet coloration with cold alcoholic potash. The following compounds have also been prepared: *salicylaldehyde hydrazone*, scarlet needles, m. p. 226°; *furfuraldehyde hydrazone*, red needles, m. p. 165—166°; *benzaldehyde hydrazone*, red needles, m. p. 166°; *phenylthiosemicarbazide*, tufts of golden-yellow needles, m. p. 188°; *allylthiosemicarbazide*, yellow needles, m. p. 168—170°; *acetylnitrotolyl hydrazine*, yellow needles, m. p. 161°.

133. "The constituents of the sandarac resins." By T. A. Henry, D.Sc.

The sandarac of commerce is the naturally exuded resin of various species of *Callitris*, usually either *C. quadrivalvis* or *C. verrucosa*.

Both varieties of resin consist of a mixture of resin acids and terpenes separable by steam distillation. From the latter, d-*pinene* has been isolated and identified. The chief volatile constituent is a diterpene, boiling at 265°, $\mu_D = 1{\cdot}5215$, $[\alpha]_D = +55°$, which behaves like a saturated substance, forming no additive compounds with bromine, hydrogen chloride, or nitrosyl chloride. Two resin acids have been isolated and examined. One of these has the composition $C_{20}H_{30}O_2$ (m. p. = 171°, b. p. 265°, 11 mm.), and closely resembles in behaviour the isomeric d-*pimaric acid* of Vesterberg (*Ber.*, 1885, **18**, 3331), but is optically inactive, and is therefore named *inactive pimaric acid*. On reduction with hydriodic acid, it gives a diterpene, $C_{20}H_{32}$. On oxidation with permanganate, pimaric acid yields acetic acid and a crystalline substance melting at 206°, which is probably *trimellitic acid*.

The second resin of sandarac has not been obtained in a crystalline form, but the highly deliquescent sodium salt and the characteristic lactone have been prepared; from analyses of these, the formula of the free acid is probably $C_{20}H_{48}O_5$. For this substance, the name *callitrolic acid* has been retained. The acid is remarkably resistant to the action of reagents, being unattacked even by hot fuming nitric acid. When heated in a vacuum, it is decomposed with the formation of carbon dioxide and a diterpene identical with that occurring naturally in the resin.

134. "Condensation of phenols with esters of the acetylene series. Part VI." By S. Ruhemann and E. Wragg, B.A.

The authors have continued the research on the interaction of phenols with ethyl chlorofumarate and ethyl phenylpropiolate, using eugenol and *m*-xylenol. From the former phenol they obtained *ethyl eugenoxyfumarate* and the corresponding acid, from which they have not been able to prepare the pyrone-compound in a pure state. *m*-Xylenol reacts with ethyl chlorofumarate to form *ethyl* m-*xylenoxyfumarate*, the acid of which, on treatment with concentrated sulphuric acid, yields 6 : 8-*dimethyl*-1 : 4-*benzopyrone*-2-*carboxylic acid* (m. p. 210° with decomposition). This, on heating, loses carbon dioxide, giving 6 : 8-*dimethyl*-1 : 4-*benzopyrone* (m. p. 80—81°). With ethyl phenylpropiolate, *m*-xylenol forms *ethyl* β-m-*xylenoxycinnamate*, which is hydrolysed by alcoholic potash to the acid. This yields, on heating,

m-xylenoxystyrene, and is decomposed by sulphuric acid into carbon dioxide, acetophenone, and *m*-xylenol.

The authors have attempted to ascertain whether only the phenyl group in the aryl ethers of the unsaturated hydroxy-acid prevents the condensation to the pyrone compound taking place, and have found that *β-phenoxycrotonic acid*, $CH_3 \cdot C(O \cdot C_6H_5) : CH \cdot CO_2H$, on heating, loses carbon dioxide and yields *β-phenoxypropylene*, $CH_3 \cdot C(O \cdot C_6H_5) : CH_2$ (b. p. 170°), and with sulphuric acid it breaks up into carbon dioxide, acetone, and phenol. To determine whether the condensation to the 1 : 4-benzopyrone compound depends upon the configuration of the aryl ethers of the hydroxy-acid, the authors have treated ethyl *β-iso*chlorocrotonate instead of its stereoisomeride with sodium phenolate; they find, however, that the same substance is formed as when ethyl *β*-chlorocrotonate is used.

135. "The hydrobromides of undecylenic acid." By J. Walker and J. S. Lumsden.

When hydrobromic acid is added to undecylenic acid, a bromo-undecylic acid, m. p. 51°, is formed at the same time as Brunner's acid, m. p. 35°. It is shown that the former is ω-bromo-undecylic acid, $CH_2Br \cdot (CH_2)_9 \cdot CO_2H$, and not Brunner's acid as was previously supposed.

136. "Normal decane-dicarboxylic acid." By J. Walker and J. S. Lumsden.

This acid was prepared by electrosynthesis from pimelic acid and was found to be identical with an acid prepared from ω-bromo-undecylic acid. The solubility in water differs entirely from the solubility of the acids described by Nördlinger and Komppa.

137. "Action of the chlorides of phosphorus on certain aromatic ethers of glycerine." By D. R. Boyd.

The author has studied the behaviour of symmetrical diphenyl glycerol-ether and some similar compounds when treated with the pentachloride and trichloride of phosphorus respectively.

Phosphorus pentachloride with diphenyl-glycerol-ether yields *β*-chlorotrimethylene-glycol-diphenyl-ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot O \cdot C_6H_5$, m. p. 37°. Phosphorus trichloride and diphenyl-glycerol-ether give a product which, on treatment with water, yields glyceryl-diphenyl-ether-phosphorous acid, $C_6H_5 \cdot O \cdot CH_2 \cdot \underset{O \cdot P(OH)_2}{CH} \cdot CH_2 \cdot O \cdot C_6H_5$, m. p. 119—120°.

Phenyl-*p*-tolyl-glycerol-ether, $C_6H_5\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_7H_7$, m. p. 73·5—76°, which is obtained by the action of phenyl-glycide ether on *p*-cresol, yields *β*-chloro-trimethylene-glycol-phenyl-*p*-tolyl ether, $C_6H_5\cdot O\cdot CH_2\cdot CHCl\cdot CH_2\cdot O\cdot C_7H_7$, m. p. 60°, and glycerol-phenyl-*p*-tolyl-ether phosphorous acid, $C_6H_5\cdot O\cdot CH_2\cdot \underset{O\cdot P(OH)_2}{CH}\cdot CH_2\cdot O\cdot C_7H_7$, m. p. 106—107°.

Further, di-*p*-tolyl-glycerol-ether yields *β*-chloro-trimethylene-glycol-di-*p*-tolyl ether, $C_7H_7\cdot O\cdot CH_2\cdot CHCl\cdot CH_2\cdot O\cdot C_7H_7$, m. p. 70°, and glyceryl-di-*p*-tolyl-ether-phosphorous acid, m. p. 111—112°.

138. "The autofermentation and liquefaction of pressed yeast." By A. Harden and S. Rowland.

The time required for the liquefaction of pressed yeast is greatly diminished by rise of temperature, whilst the rate of evolution of carbon dioxide is greatly increased. The evolution of gas ceases as soon as the yeast becomes liquid and hence is small at 50°, owing to the rapid liquefaction of the mass (1—1½ hours), whilst the total volumes evolved at 39° and 26° do not differ greatly although the times required for liquefaction are 5 and 53 hours respectively. At 14° the time required is 16 days, the rate of evolution being extremely slow, and the total volume evolved about 75 per cent. of that produced at 26°. Alcohol is produced simultaneously, the process being apparently a true alcoholic fermentation of the glycogen of the cell. Microscopic examination shows that as the evolution of gas proceeds the glycogen disappears and the vacuole of the cell increases in size. Finally, the vacuolar contents are discharged and the cell appears shrunken and irregular in outline, whilst the protoplasmic contents are highly granular.

In the presence of oxygen, a process of oxidation accompanies the evolution of carbon dioxide, a considerable rise of temperature being produced and the total volume of carbon dioxide increased. When exposed to a continuous current of oxygen, a sample of yeast was found to lose 26 per cent. of its carbon.

139. "Non-existence of the so-called suboxide of phosphorus. Part II." By C. H. Burgess and D. L. Chapman.

Substances obtained according to the methods described by Michaelis and Pitsch (*Ann.*, 1899, **310**, 45) and Michaelis and v. Arend (*Ann.*, 1901, **314**, 259) have been prepared and analysed, and shown to contain such a large amount of hydrogen that they cannot be regarded as a suboxide, but as red phosphorus containing hydrogen compounds.

The authors show that some of the analytical results of Michaelis and Pitsch indicate that the substances prepared by them contained water, and that the proof of the absence of hydrogen in the substance, described by them as a pure suboxide, is inconclusive.

As red phosphorus is easily soluble in aqueous alcoholic potash, with formation of a red solution, red phosphorus resembles in this respect the so-called sub-oxide.

The authors conclude that both the properties and the analytical results support the view that the substances hitherto described as sub-oxides of phosphorus are only impure forms of amorphous phosphorus.

140. "The action of ammonia on metals at high temperatures." By G. T. Beilby and G. G. Henderson.

Platinum, gold, silver, copper, iron, nickel and cobalt have been exposed to the action of ammonia at temperatures ranging from 400° to 900°. In every case the physical effect of the treatment was to disintegrate the metal completely, whilst a large proportion of the ammonia was resolved into its elements. The fracture of metals which have been exposed to this action is spongy or cellular; under the microscope the metal appears as if it had been suddenly cooled whilst in a state of active effervescence. The penetration of the ammonia molecules into the metal is remarkably quick if the conditions are favourable.

The authors believe that the physical effects which result from the action of ammonia upon metals at high temperatures are due to the alternate formation and dissociation of nitrides taking place between certain narrow limits of temperature, the reaction going in one direction or the other according as ammonia or hydrogen molecules preponderate in the gases which are in contact with the molecules of the metal at and below the surface. In several cases the formation of nitrides has been definitely proved. The absorption of small quantities of nitrogen by pure iron renders it hard and brittle like steel.

141. "The condensation of benzil with dibenzyl ketone." By G. G. Henderson and R. H. Corstorphine, B.Sc.

Benzil and dibenzyl ketone readily condense when warmed with excess of aqueous potash, and *tetraphenylcyclopentenolone* is produced. It melts at 208°, is readily soluble in benzene but only sparingly so in alcohol. It yields an *oxime*, m. p. 167°, which when heated in alcoholic

solution with *p*-bromophenylhydrazine gives a crystalline *hydrazone* melting at 169°. The *acetyl* derivative melts at 218°. Tetraphenyl*cyclo*pentenolone quickly reduces potassium permanganate, does not combine with bromine, but is slowly converted into a very unstable *bromine* derivative. When cautiously oxidised in the cold with chromic anhydride dissolved in glacial acetic acid, tetraphenyl*cyclo*pentenolone gives benzoic acid and a neutral *compound*, $C_{28}H_{20}O_4$, possibly *iso*benzil, $\begin{matrix}Ph\cdot C\cdot O\cdot COPh\\ \|\\ Ph\cdot C\cdot O\cdot COPh\end{matrix}$, colourless crystals, m. p. 164—165°.

Tetraphenyl*cyclo*pentenolone undergoes partial reduction when boiled for an hour or two under a reflux condenser with hydriodic acid and red phosphorus, but the product is not tetraphenyl*cyclo*pentenone, but a *tetraphenyl*cyclo*pentenol*, which crystallises in colourless needles, m. p. 162°, is readily soluble in benzene, very sparingly so in alcohol; it quickly decolorises potassium permanganate in alkaline solution. It does not react either with hydroxylamine or with phenylhydrazine, but gives an *acetyl* derivative, colourless tablets, m. p. 181°. Bromine converts it into a *bromine* derivative, $C_{29}H_{22}BrOH$, colourless needles, m. p. 215°. By treatment with phosphorus pentachloride or alcoholic hydrogen chloride it yields a *mono-chlorotetraphenyl*cyclo*pentene*, $C_{29}H_{23}Cl$, colourless prisms, m. p. 181°.

When heated at 180° in a sealed tube with hydriodic acid and red phosphorus, tetraphenyl*cyclo*pentenol is reduced to two hydrocarbons, $C_{29}H_{24}$ and $C_{29}H_{26}$, which can be separated by means of ether, in which the former is easily and the latter somewhat sparingly soluble. From its mode of formation the former is no doubt 1:2:4:5-*tetraphenyl*cyclo*pentene*, $\begin{matrix}Ph\cdot C\\ Ph\cdot CH\cdot CHPh\end{matrix}\!\!=\!\!\begin{matrix}CPh\\ \\ \end{matrix}\!\!>CH_2$. The other hydrocarbon is obtained in colourless crystals from alcohol. It melts at 80·5—81°, and is apparently identical with the 1:2:4:5-tetraphenyl*cyclo*pentane, $\begin{matrix}Ph\cdot CH\cdot CHPh\\ |\\ Ph\cdot CH\cdot CHPh\end{matrix}\!\!>CH_2$, already prepared by Wislicenus in a different manner. The former melts with decomposition at over 300°, and the latter at 80·5—81°.

142. "The chlorodibromo- and dichlorobromo-benzenes." By W. H. Hurtley, D.Sc.

Twelve tri-substituted chlorobromobenzenes should exist according to theory. The two symmetric compounds have been obtained by Hantzsch, Schleissing, and Jäger (*Ber.*, 1897, 30, 2334), the 1-chloro-3:5-dibromobenzene from 3:5-dibromoaniline. The author has prepared all the twelve compounds from anilines of known constitution, many of which have not previously been obtained. The asymmetric compounds were prepared from dihalogen anilines, by replacing the amino-

group by chlorine or bromine by Gattermann's method (*Ber.*, 1890, 23, 1222), and by eliminating the amino-group from asymmetric trihalogen anilines. The symmetric compounds resulted from the symmetric trihalogen anilines by eliminating the amino-group. The vicinal compounds were obtained from vicinal trihalogen anilines, also by eliminating the amino-group.

All the trichlorobromobenzenes are solids: the vicinal crystallise in well defined rhombic plates; the symmetric, in long slender prisms; and the asymmetric, in short thin prisms. All are very soluble in benzene, ether, chloroform, and petroleum, but less so in alcohol, from which they can be readily crystallised. The vicinal and symmetric compounds are easily volatile in steam, whilst the asymmetric are much less so.

Asymmetric; 1:2-*dichloro*-4-*bromobenzene*, prisms, m.p. 24·5°, b.p. 237°; 1:3-*dichloro*-4-*bromobenzene*, prisms, m. p. 25°, b. p. 235°; 1:4-*dichloro*-2-*bromobenzene*, prisms, m. p. 33°, b. p. 235°; 1-*chloro*-3:4-*dibromobenzene*, prisms, m. p. 35·5°, b. p. 256°; 1-*chloro*-2:4-*dibromobenzene*, prisms, m. p. 27°, b. p. 258°; 1-*chloro*-2:5-*dibromobenzene*, prisms, m. p. 40·5°, b. p. 259°.

Symmetric; 1:3-*dichloro*-5-*bromobenzene*, slender prisms, m. p. 77·5°, b. p. 232°; 1-*chloro*-3:5-*dibromobenzene*, slender prisms, m. p. 99·5°, b. p. 256°.

Vicinal; 1:2-*dichloro*-3-*bromobenzene*, rhombic plates, m.p. 60°, b. p. 243°; 1:3-*dichloro*-2-*bromobenzene*, rhombic plates, m. p. 65°, b. p. 242°; 1-*chloro*-2:6-*dibromobenzene*, rhombic plates, m. p. 69·5°, b. p. 265°; 1-*chloro*-2:3-*dibromobenzene*, rhombic plates, m. p. 73·5°, b. p. 264°.

The following new anilines and anilides were also obtained:—3:6-*dichloro*-4-*bromoaniline*, needles, m. p. 91° and its *acetyl* derivative, prisms, m. p. 189°; 2:3-*dichloro*-4-*bromoaniline*, needles, m. p. 77·5°, and its *acetyl* derivative, prisms, m. p. 138·5°; 2:4-*dichloro*-5-*bromoaniline*, flattened prisms, m. p. 86°, and its *acetyl* derivative, prisms, m. p. 192°; 2:4-*dichloro*-3-*bromoaniline*, plates, m. p. 78°, and its *acetyl* derivative, prisms, m. p. 138°; 3:5-*dichloro*-4-*bromoaniline*, needles, m. p. 129°, and its *acetyl* derivative, short prisms, m. p. 220°; 3-*chloro*-4:6-*dibromoacetanilide*, prisms, m. p. 174°; 3-*chloro*-2:4-*dibromoaniline*, plates, m. p. 88°, and its *acetyl* derivative, prisms, m. p. 152°; 2-*chloro*-4:5-*dibromoaniline*, flattened needles, m. p. 93°, and its *acetyl* derivative, needles, m. p. 193°; 2-*chloro*-3:4-*dibromoaniline*, plates, m. p. 91°, and its *acetyl* derivative, needles, m. p. 146°.

October 31st, 1901. Extra Meeting. Professor Emerson Reynolds, Sc.D., F.R.S., President, in the Chair.

Dr. Armstrong delivered the Frankland Memorial Lecture.

Frankland was born at Churchtown, Lancashire, in January, 1825. When about seven years old he went with his mother and stepfather to Lancaster, where he lived until he entered Playfair's laboratory in 1840; he there attended a private school kept by a Mr. Willasey, until he was twelve years old, when he entered the Lancaster Grammar School in the lowest class, leaving it at the age of fifteen from the highest. His mother appears to have had a great influence in developing his scientific tastes, leading him as a child to pay attention to surrounding objects; these lessons were the means of causing him to seek information about natural phenomena for himself in books. Before he was twelve, he had read many books on chemistry, electricity, and magnetism, among others, Priestley's Researches on electricity. He thus learnt how to make a Volta's pile, with which he decomposed water; and having obtained a magnet, made most of the experiments of which he had read. His master appears to have encouraged him—for on hearing that he was showing experiments to his school-fellows, he invited him to bring his apparatus into the class room and demonstrate to the school. When about twelve years old he had a strong inclination for a mechanical trade, and having access to a cabinet-maker's workshop, acquired no slight skill. Mr. Willasey, however, dissuaded him, and awakened his ambition by telling him that he ought to aim at becoming a doctor: but as his parents were led to suppose that to give him a medical training was beyond their means, on leaving school he was apprenticed to a druggist in Lancaster. The six years he spent in this capacity were years of the hardest labour. His master not only never attempted to teach him anything, but did his best to hinder his scientific advance. But Frankland's ardour was not to be damped: by rising at four, he managed to get one hour and a half for botanical work before the day's toil began. During the three years he was at the Lancaster Grammar School, he was able to carry on chemical experiments in a laboratory fitted up in the house of a school friend; and as an apprentice he enjoyed the friendship of two men—Mr. Christopher Johnson, M.R.C.S., and Dr. James Johnson, who advised him what to read and lent him apparatus, the latter even fitting up a laboratory in which Frankland and other druggists' apprentices in the town spent their evenings, Mr. Johnson occasionally telling them of Dalton's work, which was then going on.

It was on Mr. Johnson's advice that Frankland entered Playfair's laboratory in 1845. Playfair had then just been appointed organic

chemist to the Government Department of Woods and Forests, of which the Geological Survey was a branch. Before six months had passed, Playfair made him his assistant at the College for Engineers, Putney; later on, early in 1847, he became Playfair's chief assistant. Meanwhile he had been offered the post of Professor of Chemistry in the Royal Agricultural College, Cirencester, and had decided to accept the office; but a difficulty arising, and acting on the advice of Kolbe, then one of Playfair's assistants, he decided instead to go to Germany. Kolbe and he went together to Marburg in May, 1847. In the autumn he returned to England to take up the position of lecturer on botany, chemistry, and geology at Queenwood College, Hants. There he met Tyndall, and so great was the ardour of the two young men that they rose at four and taught each other until eight o'clock before doing their work in the school. He returned to Germany again to work with Bunsen in October, 1848, Tyndall, who at that time thought of becoming a chemist, accompanying him. He took the degree of Ph.D. in June, 1849, and shortly afterwards became engaged to Fräulein Fick, whom he married in 1851. In August, 1849, he went to Giessen to work in Liebig's laboratory. At Christmas he left for Berlin, intending to work with Rose, but receiving there the offer of the chair vacated by Playfair at the Putney College, he returned home. He remained at Putney until January, 1851, when he became Professor of Chemistry at Owens College, Manchester. In October, 1857, he returned to London as lecturer on chemistry in St. Bartholomew's Hospital. In 1863, he resigned this post to become Professor of Chemistry in the Royal Institution. In 1865, he succeeded Hofmann at the Royal College of Chemistry and Royal School of Mines, a post which he held until he retired in 1885. Meanwhile, in 1868, he had been appointed a member of the Rivers Pollution Commission. He died on August 9, 1899.

Frankland began research work with Kolbe very few months after entering Playfair's laboratory; before they left for Germany—within eighteen months of his having commenced to study chemistry systematically—they had completed their work on the hydrolysis of the nitriles, which led to the determination of the constitution of the great group of acids now known as carboxylic acids. They had begun to study the action of potassium on ethyl cyanide with a view to isolating ethyl; this work was completed in Marburg, and Frankland made his maiden appearance as reader of a paper before the Chemical Society in communicating the results which Kolbe and he had obtained. As soon as he was installed at Queenwood, he began independent work and sought to isolate the alcohol radicles. On continuing this research, on the occasion of his second visit to Bunsen's laboratory, he soon succeeded in preparing "ethyl" and "methyl," and in the course of these ex-

periments made the all important discovery of zinc methyl and ethyl. The amyl compounds were studied in Liebig's laboratory. At Putney he continued his work on organo-metallic compounds; and it was here that he studied the action of chlorine on stannethyl, &c., and was first led to discover the law of valency; this work was completed at Manchester: the memoir in which Frankland formulated the doctrine which must hereafter always be associated with his name was read to the Royal Society on June 17, 1852.

Besides giving an account of Frankland's early education and subsequent career and considering his character, Dr. Armstrong entered somewhat fully into an analysis of the work he did with Kolbe; he then proceeded to consider his investigations relating to the isolation of the hydrocarbon radicles and his researches on the organometallic compounds, which culminated in the discovery of the doctrine of valency, leaving the vast mass of work—chemical and physical—which he did subsequently to be dealt with in the printed memoir. Attention was called to the great importance of Frankland and Kolbe's work on the acids of the acetic series. The two papers in which their results are described were referred to as deserving to rank as classics, as specimens of highly original and clearly reasoned precise argument, as well as on account of the importance of the results they disclosed. That they were in no way appreciated at the time of publication was due to the extraordinary hold which Gerhardt's type-system had obtained. For a like reason, Frankland's statement of the doctrine of valency produced originally but a slight impression, and it was only at a later stage—owing to the use that Kekulé had made of it in discussing the constitution of carbon compounds, benzene especially—that its importance became recognised, and it became the guiding principle: and even then Frankland's services were to a great extent overlooked. It was beyond the power of his contemporaries, in fact, to appreciate the bearings of his discoveries when they were first made known: and when the wave of Gerhardtism had spent its force, they appeared almost commonplace, so great had been the advance in knowledge meanwhile and so insensibly had Frankland's ideas crept into their minds. Reasons were fully stated which appear to justify the belief that Kekulé must have derived his inspiration from Frankland, who alone is to be regarded as the discoverer of the doctrine of valency—Kekulé's great work having been to develop the consequences of its application to carbon compounds.

Taking the whole of Frankland's work into account, it constitutes a record which is altogether remarkable as evidence of his originality, of the catholic character of his interests, of his practical ability and of his vigour: it must serve to place him in the very highest rank among the chemists of the century, whilst his early work entitles him to be

regarded as one of the great pioneers in establishing the modern doctrine of constitution.

On the motion of Professor ODLING, seconded by Sir H. E. ROSCOE, a vote of thanks was passed to Dr. Armstrong for his lecture.

November 7th, 1901. Professor MCLEOD, F.R.S., Vice-President, in the Chair.

Messrs. W. Lowson, E. Neumann, A. Findlay, E. Horton, G. Tatam, G. W. F. Holroyd, and S. E. Sheppard were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Thomas Allen, 15, Sea View Terrace, Hartlepool; Arthur Baker, 130, Walmersley Road, Bury, Lancashire; Walter Craven Ball, 19, Lewisham Hill, S.E.; Andrew Russell Bennet, 1, Wildman Street, Nottingham; Harding Bickford, 46, Currie Street, Adelaide, S. Australia; Henry Boyers, 20, Knox's Street, Sligo; William Burton, Cotleigh, Nunnery Fields, Canterbury; William Cormack, 3, Westfield Place, Eskbank, Midlothian; Frank Crossley, Duchy Bank, Seedley Road, Pendleton, Manchester; John Howard Davidson, Golden Hill, Stoke-on-Trent; Francis Davis, Whitwell, Elland, Yorks; Robert English, 8, Colwall Villas, Burley Road, Beckenham, Kent; Eugène Arthur Fasnacht, Clayton Mount, Newton Heath, Manchester; Henry Wippell Gadd, 42, Union Road, Exeter; Hermann Charles Thomas Gardner, London Hospital, E.; Edward Gillman, Barbados, West Indies; William Peer Groves, Oldfield Hall, Altrincham, Manchester; Herbert Harding, 20, Stratford Road, Kensington, W.; Beresford Ingram, 19, Lewisham Hill, Lewisham, S.E.; Walter Henry Jollyman, Spartan House, Colney Hatch Lane, Muswell Hill, N.; James David Kettle, 1, Vardens Road, St. John's Hill, S.W.; Julian Bruce Kingsmill, Ordnance College, Woolwich; Alfred Tabois Larter, 184, Holland Park Avenue, W.; Peter Macdonald, Lapstone Road, Millom, Cumberland; Lewis Jenkin Meyrick, 137, City Road, Birmingham; Charles Killick Millard, The Gilroes, Groby Road, Leicester; Albert Edward Parkes, 43, Whitehorse Street, Stepney, E.; Charles James Tomlin Pollitt, Athole, Church Street, Croydon, Sydney, N.S.W.; Charles Leonard Royle, Nellikuppam, South Arcot, India; John Henry Ryffel, 10, Onslow Gardens, Highgate, N.; George Charlton Scott, Eston Grange, Grangetown, R.S.O., Yorks; Edward Charles Sher-

wood, 39, Vincent Square, Westminster, S.W.; Norman Smith, 15, King Street, Bury; William Henry Templeman, 67, Park Street, Spring Bank, Hull; Harold Fay Fleetwood Varley, 22, Strathblaine Road, New Wandsworth, S.W.; Herbert George Wallace, Axim, West Africa; Philip Lewington Whitehouse, 32, Lawrence Street, Dowanhill, Glasgow.

Of the following papers, those marked * were read:

***143. "Note on the supposed formation of an oxide of hydrogen higher than the dioxide" By W. Ramsay, F.R.S.**

Bach (*Ber.*, 1900, **33**, 1506) has stated that evidence can be obtained of the existence of a peroxide of hydrogen higher than the dioxide by comparing the amount of oxygen evolved from peroxide on treatment with permanganate with the weight of the peroxide present in solution, as determined by titration with permanganate. It was suggested by Armstrong (*Proc.*, 1900, **16**, 154) that the discrepancy should be attributed to the formation of persulphuric acid and Caro's acid, due to the action of the peroxide on the sulphuric acid present during the titration. The author now showed that if peroxide be added to a mixture of sulphuric acid with permanganate, all the oxygen is evolved, but that if the permanganate be added to a mixture of peroxide with sulphuric acid, only a partial evolution of oxygen takes place, for neither persulphuric acid nor Caro's acid is readily attacked by permanganate. On the other hand, if acetic acid be substituted for sulphuric acid, the amount of oxygen evolved corresponds exactly with the amount of permanganate added, whether the latter be added to a mixture of peroxide and acetic acid, or whether the peroxide be added to a mixture of permanganate and acetic acid.

***144. "The electrolytic reduction of nitrourea." By G. W. F. Holroyd.**

Nitrourea can be reduced to semicarbazide much more easily if the reduction be effected by electrolysis than by the original method of Thiele and Heuser (*Ann.*, 1895, **288**, 311).

An aqueous solution of ammonium chloride serves as electrolyte. No porous cell is used. The reduction is effected at 20°. The poles are of iron or zinc. In the latter case, an alternating current is employed to prevent the formation of a bridge of zinc from pole to pole. Four ampere hours are required for the reduction of each gram of nitrourea. The semicarbazide is precipitated as benzalsemicarbazone. The yield of recrystallised benzalsemicarbazone is 60 per cent. of the theoretical.

***145. "The constitution of pilocarpine. Part III." By H. A. D. Jowett, D.Sc.**

On a fuller examination of the products of the oxidation of *iso*pilocarpine with permanganate, it was found that, in addition to acetic and pilopic acids, small quantities of *propionic acid* and of a new acid named *homopilopic acid*, $C_8H_{12}O_4$, are formed. The formula $C_7H_{10}O_4$, previously proposed for pilopic acid, is confirmed both by analyses of various derivatives of the acid and by the determination of the molecular weight of the methyl ester.

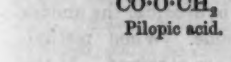
Pilopic acid, $C_7H_{10}O_4$, melts at 104° (corr.) and is dextrorotatory $[\alpha]_D^{17°} = +36{\cdot}1°$ in aqueous solution, with excess of alkali present $[\alpha]_D^{17°} = +3{\cdot}2°$. Its *methyl ester* boils at 155—160° under 10 mm. pressure, and at 275° under 757 mm. Its *barium* salt, $(C_7H_9O_4)_2Ba$, is a microcrystalline powder readily soluble in water. The *anilide*, $C_7H_9O_3NHPh$, forms white, flat, pearly plates melting at 110°. The *acid strychnine* salt, $C_{21}H_{22}O_2N_2,(C_7H_{10}O_4)_2$, is readily soluble in water and alcohol, sparingly soluble in ether, and melts at 120°. The *diamide* of the *hydroxy-acid*, $C_7H_{14}O_3N_2$, formed by the action of ammonia on ethyl pilopate, occurs in acicular crystals, sparingly soluble in cold water or alcohol, freely soluble in these solvents when hot, and melts at 160°. The *barium* salt of the *hydroxy-acid*, $C_7H_{10}O_5Ba,H_2O$, is a microcrystalline powder freely soluble in water, $[\alpha]_D^{17°} = +6{\cdot}1°$. *Homopilopic acid*, $C_8H_{12}O_4$, boils at 235—237° under 20 mm. pressure, and is dextrorotatory, $[\alpha]_D^{17°} = +45{\cdot}4°$, with excess of alkali $[\alpha]_D^{17°} = +5{\cdot}9°$. Titration of the acid showed it to be a monobasic lactonic acid. Its *ethyl ester* boils at 210° under 10 mm. pressure. The *barium* salt, $(C_8H_{11}O_4)_2Ba$, is very hygroscopic. The *diamide* of the *hydroxy-acid*, $C_8H_{16}O_3N_2$, forms well-defined prisms melting at 208°, fairly soluble in hot water, but sparingly soluble in cold or hot alcohol or cold water. The *barium* salt of the *hydroxy-acid*, $C_8H_{12}O_5Ba,H_2O$, is a microcrystalline powder stable in the air. The author showed that the piluvic acid of Pinner and Kohlhammer (*Ber.*, 1901, **34**, 727) may possibly be a mixture of homopilopic with some pilopic acid. Repetition of previous experiments on the bromination of ethyl pilopate, giving rise to the formation of *iso*butyric acid, show that this acid is the product of a secondary reaction, and that the formula previously proposed (*Trans.*, 1900, **77**, 851) must be abandoned. Pilopic acid is not easily reduced by hydriodic acid, as no change occurs on heating to 210°.

Pilopic acid, when fused with potassium hydroxide at a high temperature, yields only one product—normal butyric acid. Fusion at a lower temperature produces a small quantity of a crystalline, isomeric,

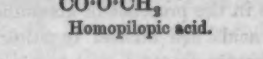
unsaturated acid melting at 190°, but the greater part of the acid is recovered unchanged.

Homopilopic acid on fusion with potash at a medium temperature yields α-ethyltricarballylic acid, $C_8H_{12}O_6$.

From a consideration of the results obtained, the following formulæ are proposed for pilopic and homopilopic acids:



Pilopic acid.



Homopilopic acid.

***146. "A new synthesis of α-ethyltricarballylic acid." By H. A. D. Jowett, D.Sc.**

α-Ethyltricarballylic acid has been synthesised by the following reactions:—

(1) *Ethyl β-ethylcyanosuccinate* was prepared by condensing the sodium compound of ethyl cyanacetate with ethyl α-bromobutyrate (compare Bone and Sprankling, *Trans.*, 1899, 75, 839).

(2) The sodium compound of ethyl β-ethylcyanosuccinate was condensed with ethyl bromoacetate with formation of ethyl α-ethyl-β-cyanotricarballylate. This reaction may be represented by the equation

$$CH_2BrCO_2Et + CO_2Et\cdot C(CN)Na\cdot CH(C_2H_5)\cdot CO_2Et = CO_2Et\cdot CH_2\cdot C(CN)(CO_2Et)\cdot CH(C_2H_5)\cdot CO_2Et + NaBr.$$

(3) *Ethyl ethylcyanotricarballylate* was hydrolysed with sulphuric acid; the resulting acid, heated at 180°, gave α-ethyltricarballylic acid.

Ethyl β-ethylcyanosuccinate, $CO_2Et\cdot C(CN)H\cdot CH(C_2H_5)(CO_2Et)$, boils at 167—168° under 20 mm. pressure, and has a density of 1·0647 at 15°/15°.

Ethyl α-ethyl-β-cyanotricarballylate,

$$CO_2Et\cdot C(C_2H_5)H\cdot C(CN)(CO_2Et)\cdot CH_2\cdot CO_2Et,$$

boils at 208° under 21 mm. pressure, and has a density of 1·0972 at 16°/16°.

α-Ethyltricarballylic acid, $CO_2H\cdot C(C_2H_5)H\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, melts at 157°, the figure previously given by Michael (*Ber.*, 1900, 33, 3745). The following new derivatives have been prepared:—The *anhydro-acid*, $C_8H_{10}O_5$, could only be obtained amorphous, and yields an amorphous compound with aniline; the *triethyl ester* is a colourless, limpid liquid boiling at 170—175°. The *barium* salt, $(C_8H_9O_6)_2Ba_3,7H_2O$, is crystalline, and is more soluble in cold than in hot water. Only 6 molecules of water of crystallisation are lost at 180°. The *calcium* salt, $(C_8H_9O_6)_2Ca_3,9H_2O$, is characteristic, as its

aqueous solution, on heating to 100°, becomes a firm jelly which liquefies on cooling. The *copper* salt, $(C_8H_9O_6)_2Cu_3.5H_2O$, is a greenish-blue powder.

***147. "The benzoylation of fatty acids in the presence of ammonia; formation of amides." By K. J. P. Orton.**

On treating many monobasic fatty acids with excess of benzoyl chloride in the presence of ammonia and sodium hydroxide, the amides of the acids are formed together with benzamide. When methylamine is substituted for ammonia, methylamides are obtained. If the fatty acid and benzoyl chloride are heated together at 100—120° for 2 or 3 hours before treating with ammonia (or methylamine) and sodium hydroxide, the yield of amide is much increased and amounts in some cases to as much as 75 per cent. of the acid used. When the acids possess hydroxyl or amino-groups, they are at the same time both benzoylated and converted into amides.

The following amides have been prepared by this method: Phenylacetamide; *p*-nitrophenylacetamide; p-*nitrophenylacetmethylamide*, $C_6H_4NO_2{\cdot}CH_2{\cdot}CONHMe$, crystallises in long, silky, colourless needles (from water) m. p. 159°; p-*benzaminophenylacetamide*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CONH_2$, prepared from *p*-aminophenylacetic acid, crystallises from alcohol in small plates, m. p. 248°; p-*benzaminophenylacetic acid*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$, prepared by the Schotten-Baumann method, forms tufts of needles, m. p. 205—206°; p-*benzoxyphenylacetamide*, $C_6H_5{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CONH_2$, prepared from *p*-hydroxyphenylacetic acid, forms insoluble, microscopic crystals, m. p. 167—169°; *benzoylmandelic amide*, $C_6H_5{\cdot}CH(O{\cdot}CO{\cdot}C_6H_5){\cdot}CONH_2$, prepared from mandelic acid, crystallises from water in tufts of silky needles, m. p. 162°; and *benzoylmandelic methylamide* in needles, m. p. 139°; *cinnamic methylamide*, $C_6H_5{\cdot}CH{:}CH{\cdot}CONHMe$, crystallises from water in plates, m. p. 111°; *dibromocinnamic methylamide* crystallises in lustrous prisms, which become coloured above 200°, melt and decompose at 214°. *Dibenzoyltyrosinamide*,

$$C_6H_5{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH{\cdot}CO{\cdot}C_6H_5){\cdot}CONH_2,$$

prepared from tyrosin, crystallises in aggregates of lustrous needles, m. p. 246°. Stearic amide is obtained from stearic acid.

It is probable that either a compound anhydride of benzoic and the fatty acid (or possibly a simple anhydride of the fatty acid) is first formed; with ammonia (or methylamine) the anhydride yields the amide of the fatty acid.

***148. "Liquid nitrogen peroxide as a solvent." By P. F. Frankland, Ph.D., F.R.S., and R. C. Farmer, M.Sc., Ph.D.**

A study of the properties of this liquid led to the following results. Inorganic salts are not dissolved by nitrogen peroxide, and in most cases are unattacked. The liquid is a powerful solvent for organic compounds. It is a moderately inert reagent, but its activity is greatly increased by the presence of traces of water or of lower oxides. Most organic acids, as well as halogen and nitro-compounds and quinones, could be dissolved unchanged and recovered by evaporation. Hydroxy-compounds were generally, though not always, attacked, phenol being converted to 2 : 4-dinitrophenol. Aniline derivatives were diazotised and some compounds were merely oxidised, as anthracene, which was completely converted into anthraquinone.

The electric conductivity of hydrochloric acid, as well as of a number of organic acids, was examined in this solvent and found to be too small to be measured, showing that the liquid does not bring about electrolytic dissociation. A number of molecular weight determinations of dissolved substances were made by the ebullioscopic method. The constant for 1 gram-molecule in 100 grams of solvent was first determined by a series of experiments in which indifferent compounds (nitrobenzene, &c.) were used and found to be equal to 13·7. On extending the experiments to organic acids, these were found in many cases to be associated to double molecules. This was found to hold for acetic and benzoic acids and for several of their derivatives. Di- and tri-nitrophenol, on the other hand, gave their normal molecular weights.

***149. "On an incrustation from the Stone Gallery of St. Paul's Cathedral." By E. G. Clayton, F.I.C.**

Around what is known as the Stone Gallery, at the base of the dome of St. Paul's Cathedral, is a balustrade of Portland stone, surmounted by a heavy coping-stone of the same material. Much of the surface of the stone is greatly "weathered," and is coated by a stratum of a grey or black substance, which in some places (especially on the under-side of the coping-stone) attains a thickness of three-quarters of an inch. This material, which is brittle and detachable with a knife, has a very rough and irregular surface, is stalagmitic in character, and, though differing in colour, in other respects resembles very closely some boiler deposits. It can easily be reduced to a fine, grey powder, which, under the microscope, shows no morphological features indicating the presence of fungoid or similar matter.

Some of this incrustation has been analysed, with the following results.

In 100 parts by weight:

Water, lost at 100°	2·06
„ „ 150°	22·48
Organic matter (carbon)	1·10
Lime	26·44
Magnesia	0·27
Ferrous oxide	1·31
Silica, sand, &c.	10·39
(Including combined silicic acid, SiO_2, 2·33)	
Sulphuric acid (combined)	34·93
Phosphoric acid „	1·02
Carbonic „	none
Chlorine	trace
	100·00

Bases and radicles being combined, the composition is apparently as follows:

Water (100°)	2·06
„ (150°)	22·48
Carbon (soot)	1·10
Calcium sulphate	59·38
„ phosphate	2·22
„ silicate	1·63
Magnesium silicate	0·67
Iron silicate	2·40
Sand and uncombined silica	8·06
	100·00

Evidently, therefore, the substance is composed chiefly of calcium sulphate, hydrated, together with some siliceous matter. Calcium carbonate, which might have been expected to be present, is not one of the constituents. What, then, is the origin of the incrustation? In the immediate vicinity, there is no obvious source of gypsum or plaster. It cannot have been blown upwards from the bare leaden roof of the Cathedral or floor of the gallery. The stones of the balustrade are cemented, of course, with mortar. Still less likely is it that so much calcium sulphate has found its way from the neighbouring thoroughfares. The sand and soot may, to a great extent, be thus derived, and perhaps a small proportion of the calcium sulphate represents coal-ash transported by wind. But after a careful consideration of all the circumstances, and especially the characteristic

appearance of the incrustation, it is suggested that the presence of the main component is principally due to two centuries' solvent and weathering action of rain, charged with sulphurous and sulphuric acids derived from the gases and smoke of innumerable surrounding chimneys. The action exerted by rain beating heavily against the stone, in that exposed situation, must be very considerable. The deposit of calcium sulphate, left by the water dripping and running from the under-side of the coping-stone, has become gradually thicker, just as is the case with stalagmite and calcareous tufa, to which the external features of the incrustation give it a curiously close resemblance. That the weathering influence of rain has been potent, no one examining the surface of the Portland stone can have a moment's doubt.

150. "Note on asbestos." By E. G. Clayton, F.I.C.

The following analyses of four kinds of asbestos (one of which, A, was stated to be of English origin, the remainder being examples of the ordinary mineral) are recorded for information and comparison, no published analysis of asbestos of English origin having been observed by the writer in any scientific journal.

Including the English specimen, all possess the general composition distinctive of true amphibole-asbestos, rather than asbestiform serpentine or chrysotile, which contains much more water and little or no lime. The English mineral consisted of moderately long, greyish-green fibres, easily separable, and in appearance resembling Italian asbestos, though characterised by unusual brittleness. B, C, and D, which had been pulverised before reaching the writer, were apparently associated with a little gypsum:

	A.	B.	C.	D.
Water lost at 100°	1·19	0·37	0·86	—
,, ,, 150°	0·05	0·13	0·00	—
,, ,, a red heat	0·70	0·95	1·83	—
Total water	1·94	1·95	2·69	1·39
Silica (with traces of manganese oxide, alkalis, &c.)	60·88	48·48	59·82	61·74
Lime	11·11	6·19	5·91	6·91
Magnesia	10·84	35·52	28·27	25·72
Alumina	trace	4·69	1·25	2·30
Iron oxide	15·23			
Sulphuric anhydride	—	3·17	2·06	1·94
	100·00	100·00	100·00	100·00

151. "The action of nitric acid on methyl dimethylacetoacetate. Preliminary notice." By W. H. Perkin, Ph.D., F.R.S.

When methyl dimethylacetoacetate is heated with nitric acid of sp. gr. 1·4—1·45, vigorous action sets in, and if, when this has subsided, the product is thrown into water, a yellow oil separates which on standing becomes semi-solid owing to the deposition of crystals. The crystalline product, when collected and purified by crystallisation from alcohol, melts at 65° and gives numbers on analysis agreeing with those required for the formula $C_{14}H_{18}O_8N_2$. This new substance is decomposed by alkalis with formation of dimethylmalonic acid, *iso*-butyric acid, hydrogen cyanide, carbon dioxide, and ammonia, and when treated with ammonia gives dimethylmalonamide. Its composition appears to be expressed by the formula $\begin{matrix} O\cdot N:C\cdot CO\cdot C(CH_3)_2\cdot CO_2CH_3 \\ | \\ O\cdot N:C\cdot CO\cdot C(CH_3)_2\cdot CO_2CH_3 \end{matrix}$.

It reacts with semicarbazide, yielding a crystalline substance of the composition $C_{16}H_{24}O_8N_8$.

When the substance melting at 65° is reduced with tin and hydrochloric acid, it yields two colourless substances melting at about 154° and 173°, as well as a third substance which melts at 177° and crystallises in primrose-yellow needles.

The two colourless substances are isomeric and have the composition $C_{14}H_{20}O_8N_2$; the one melting at 154° gives a crystalline condensation product on treatment with semicarbazide, whereas the other, melting at 173°, does not.

The primrose-yellow substance (m. p. 177°) has the formula $C_{12}H_{16}O_5N_2$, and is much less soluble in alcohol than the colourless reduction products. It combines with semicarbazide and with phenylhydrazine. It dissolves in potassium hydroxide, forming an intense orange-red solution from which a colourless, crystalline acid, $C_{12}H_{14}O_5N_2$, separates on adding a mineral acid. This acid melts at 214°, yields a well characterised barium salt, $(C_{12}H_{13}O_5N_2)_2Ba$, and is reconverted by treatment with methyl alcohol and hydrochloric acid into the primrose-yellow substance, which is therefore its methyl ester. The constitution of the three reduction products will be considered in the detailed paper.

Substances similar in constitution to that obtained by the action of nitric acid on methyl dimethylacetoacetate have already been prepared in the aromatic series, thus Hollemann (*Ber.*, 1895, **28**, 3360) obtained diphenyldinitrosacyl, $\begin{matrix} O\cdot N:C\cdot CO\cdot C_6H_5 \\ | \\ O\cdot N:C\cdot CO\cdot C_6H_5 \end{matrix}$, by the action of concentrated nitric acid on acetophenone. Baum (*Ber.*, 1895, **28**, 3211) also obtained

a condensation product of similar constitution by treating acetylmesitylene with nitric acid.

152. "Note on the displacement of benzyl by methyl in substituted nitrogen compounds." By H. O. Jones, B.A., B.Sc.

In trying to effect the union of methyl iodide and dibenzylaniline, it was found that no action took place in the cold, but that on heating the mixture to 100° in a sealed tube only phenyltrimethylammonium iodide, unchanged dibenzylaniline and benzyl iodide were obtained (*Proc. Camb. Phil. Soc.*, 11, [ii], 114). On heating together dibenzylaniline and methyl iodide in the proportion of one molecule of the former to three of the latter to 100° for about two hours, a nearly theoretical yield of phenyltrimethylammonium iodide was obtained, the two benzyl groups having been eliminated as benzyl iodide.

It was of interest, in view of the fact that V. Meyer (*Ber.*, 1875, 8, 936) had shown that methyl iodide had no action on tetraethylammonium iodide, to see whether methyl iodide would displace the benzyl radicle in an ammonium compound. Phenylmethyldibenzylammonium iodide was therefore heated to 100° with methyl iodide, with the result that it was entirely converted into phenyltrimethylammonium iodide and benzyl iodide. The same displacement was effected in phenyldimethylammonium iodide and benzylaniline.

Experiments were made with ethyl, propyl, isobutyl, and allyl iodides on the above benzyl compounds; and with methyl iodide on other phenyl ammonium compounds; but at 100° no displacement was observed in any case.

The ready displacement of the benzyl radicle by methyl may be due to the "mobility" of the former, which is usually split off to some slight extent as iodide when a benzyl ammonium iodide is heated either in the dry state, or in aqueous or alcoholic solution, combined with the stability of phenyltrimethylammonium iodide, which is only decomposed at 220—225°. However, the non-displacement of benzyl by alkyl radicles other than methyl, and of such radicles as ethyl and propyl by methyl, suggests some peculiar relation (possibly stereochemical) existing only between the methyl and benzyl radicles.

ADDITIONS TO THE LIBRARY.

I. Donations.

Berthelot, M. Les Carbures d'hydrogène 1851—1891. Recherches expérimentales. 3 vols. T. i. L'acétylène: synthèse totales des carbures d'hydrogène. T. ii. Les carbures pyrogénès, series diverses. T. iii. Combinaison des carbures d'hydrogène avec l'hydrogène, l'oxygène, les éléments de l'eau. Paris. 1901. From the Author.

Idris, T. Howell Williams. Notes on essential oils, with special reference to their use, composition, chemistry, and analysis. With tables of constants of the more commonly occurring oils. Second edition. London. 1901. From the Author.

Phipson, Thomas Lamb. Researches on the past and present history of the earth's atmosphere, including the latest discoveries and their practical applications. London. 1901. From the Author.

Fischer, Emil, and Guth, Max. Der Neubau des Ersten Chemischen Instituts der Universität Berlin. Ill. Berlin. 1901. From Prof. Fischer.

At the next meeting, on Thursday, November 21st, the following papers will be communicated:—

"On the oxidation of sulphurous acid to dithionic acid by metallic oxides." By H. C. H. Carpenter.

"Optically active β-hydroxybutyric acids." By A. McKenzie.

"On the hydrochloride of thiocarbamide." By H. P. Stevens.

"The constituents of the essential oil of *Asarum Canadense*." By F. B. Power and F. H. Lees.

"Note on the reduction of trinitrobenzene and trinitrotoluene with hydrogen sulphide." By J. B. Cohen and H. D. Dakin.

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PROCEEDINGS

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November 21st, 1901. Professor EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

Messrs. R. Lloyd Whiteley and H. A. Tozer were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Walter Geoffrey Black, 9, Routh Road, Wandsworth Common, S.W.; Harry Burrows, The Green, Southgate, N.; Frederick Edward Catchpole, 11, Jerningham Road, New Cross, S.E.; James Ward Daniels, Westwood, Medomsley R.S.O., Co. Durham; Frederick Davis, "Stanley," Whalley, nr. Blackburn, Lancs.; Charles Dorée, 87, Gore Road, London, N.E.; Clarence J. Green, B.Sc., 24, Dalberg Road, Brixton Church, S.W.; Ernest Bowman Ludlam, University College, Bristol; Sydney Glyde Stephen Panisset, 7, Jersey Road, Strood, Rochester; William Charles Ross, 27, Pitt Street, Edinburgh; Francis Bernard Stead, Clifton College, Bristol; Arthur James Webb, 21, Hammelton Road, Bromley, Kent; Charles Edward Womersley, Kilpin Hill, nr. Dewsbury, Yorks.; and of Messrs. T. K. Gajjar, Gingaum, Bombay; J. S. Jameson, Durban, Natal; Albert William Denis Leahy, Darjeeling, India; and Walter Herbert Pay, Durban, Natal, authorised by the Council under Bye Law I (3).

EXTRAORDINARY GENERAL MEETING.

The PRESIDENT announced that he had received a requisition to summon an Extraordinary General Meeting at which it will be proposed:

(1) To change that part of Bye Law XI which now reads,

"The Ordinary Scientific Meetings of the Society shall be held twice in every month, from November to June inclusive, except in the month of January, when the Society shall meet once only and also at Easter when, if the Council see fit, there shall be only one meeting in the month; the specific days and hours of meeting to be determined by the Council."

by deleting the words "the Council" and inserting in their place the words "an Extraordinary General Meeting."

(2) That the Ordinary Meetings of the Society shall continue to take place, as heretofore, on Thursdays, at 8 p.m.

Acting under the provisions of Bye Law XIII, he therefore summoned an Extraordinary Meeting for Thursday, December 12th, at 8 p.m.

The following is the text of the above-mentioned requisition:—

To the PRESIDENT OF THE CHEMICAL SOCIETY.

SIR,

We, the undersigned Fellows of the Chemical Society, respectfully request you to summon an Extraordinary General Meeting of the Society, at the earliest possible date, for the purpose of:

(1) Proposing a modification of Bye Law XI, and
(2) Submitting a resolution.

We subjoin the terms of the proposed modification and resolution, and have the honour to remain,

Yours very faithfully,

Richard Berncastle.
R. L. Jenks.
George Harker.
T. Martin Lowry.
Walter C. C. Pakes.
Charles Mills.
H. Droop Richmond.
S. J. Peachey.
W. A. Wayland.
Alfred Wm. Harvey.
H. F. Fermor.
Arthur H. Coote.
Otto Hehner.
T. H. Page.
Edwin C. Jee.
Ernest Goulding.
Thomas A. Henry.
Geo. S. Blake.
F. B. Power.
H. A. D. Jowett.
Gerald T. Moody.
William A. Davis.
Geo. Bousfield.
Edward Horton.

Henry R. Redman.
James Moir.
Wm. J. Kemp.
G. S. Newth.
G. T. Morgan.
J. C. Philip.
Chapman Jones.
A. J. Bullen Cooper.
William Robertson.
Chas. A. West.
W. H. Merrett.
H. C. H. Carpenter
E. O. Courtman.
F. Stanley Kipping.
H. H. Robins.
W. R. Hodgkinson.
Bernard Dyer.
Edgar S. Barralet.
Samuel Rideal
T. A. Lawson.
R. J. Friswell.
J. W. Hinchley.
C. E. Browne.
F. F. Renwick.
Albert Cooper.
B. V. Storr.
P. Gerald-Sanford.
H. R. Le Sueur.
Alfred C. Chapman.
Chas. E. Beadnell.
Edgar Neumann.
H. Bailey.
Francis H. Carr.
E. Haynes Jeffers.
T. FitzGibbon.
J. Wilson.
W. T. Gilles.
Alex. Guthrie.
W. P. Dreaper.
Arthur Lapworth.
D. Northall-Laurie.
J. T. Hewitt.
F. Dixon.
A. G. Bloxam.
Edgar M. Chapman.
K. J. P. Orton.
Godfrey Melland.
T. Slater Price.
Harry Silvester.
Thomas H. Pope.
Thomas Royle.
D. A. Sutherland.

D. A. Louis.
Henry P. Stevens.
Frederic Jas. M. Page.
S. Godfrey Hall.
Bertram Blount.
Charles Watson.
Chas. E. Eastick.
Peter MacEwan.
J. Lewkowitsch.
John Heron
Charles A. Kohn.
Walter T. Reid.
Oscar Guttmann.
S. Dickson.
James H. Millar.
Sidney Williamson.
Otto Rosenheim.
Philip Schidrowitz.
J. Vargas Eyre.
F. Southerden.
W. A. Lethbridge.
G. G. Quinn.
W. T. B. Ridge.
Leonard P. Wilson.
H. Wulff Kinnersley.
W. A. Handcock.
Arthur Marshall.
William Rintoul.
John Charles Burnham.
Sidney S. Napper.
Wm. T. Thomson.
Edward W. Lewis.
W. B. Woodbridge.
B. S. Bull.
G. Cecil Jones.
Arthur E. Ekins
E. H. Fisher.
Julian L. Baker.
Jas. Grant.
John Allan.
W. C. Reynolds.
W. H. Taylor.
H. C. Sayer.
E. F. Harrison.
John E. Mackenzie.
J. F. Thorpe.
Ju. Hübner.
L. G. Radcliffe.
Thos. R. Duggan.
Wm. Chattaway.
Martin Priest.
(name illegible).

It is proposed :—

(1) On line 7 of Bye Law XI (page 21, fifth line from top) to delete the words "the Council" and insert in their place the words "an Extraordinary General Meeting of the Society."

(2) To resolve that the Ordinary Meetings of the Society shall continue to take place, as heretofore, on Thursdays, at 8 p.m.

Of the following papers, those marked * were read:

***153. "On the hydrochloride of thiocarbamide." By H. P. Stevens.**

The hydrochloride of thiocarbamide, CSN_2H_4,HCl, may be obtained directly by dissolving thiocarbamide in an excess of warm concentrated hydrochloric acid. On cooling, the salt separates out in large compact crystals, which have a strongly acid reaction, melting, with decomposition, below 100°, and are readily soluble in water and alcohol. They react with the latter solvent when warmed to form, probably, in the first case, ethyl chloride which, combining directly with thiocarbamide, yields the hydrochloride of ethyl-pseudo-thiocarbamide in white prisms.

The method of Glutz for the preparation of thiocarbamide hydrochloride yields a very impure product, due partly to loss of hydrochloric acid on concentration and partly to the salt reacting with alcohol during recrystallisation.

***154. "The constituents of the essential oil of Asarum Canadense." By F. B. Power and F. H. Lees.**

In a previous investigation of this oil by one of the authors (Power, *Inaug. Diss. Strassburg*, 1880; *Proc. Amer. Pharm. Assoc.*, 1880, 28, 464) it was found to contain a terpene, $C_{10}H_{16}$; two fragrant alcohols, b. p. 196—199° and 222—226°, both having the composition $C_{10}H_{18}O$; a nearly inodorous body, b. p. 254—257°, which, on oxidation with chromic acid, afforded a crystalline acid, $C_9H_{10}O_4$, the latter having since been shown to be veratric acid by Petersen (*Ber.*, 1888, 21, 1062), who has also identified the substance affording it as methyleugenol; a deep blue oil collected at 275—350°; a large amount of acetic acid combined with the alcohols of the oil in the form of esters, and a very small amount of a less soluble oily acid which was believed to contain valeric acid.

The present investigation has shown the oil to have a much more complex composition than was at first supposed. The authors have now identified the following compounds, most of them by well-defined crystalline derivatives. (1) A phenol, $C_9H_{12}O_2$, having a creosote-like odour; (2) pinene (nitrosochloride, m. p. 103—104°, and nitrolpiperidine, m. p. 118—119°); (3) *d*-linalool (citral and citryl-β-naphthocinchoninic acid, m. p. 195—198°); (4) *l*-borneol (camphor, m. p. 175°, $[\alpha]_D = -40{\cdot}3°$, and oxime, m. p. 115—116°); (5) *l*-terpineol (a keto-

lactone, $C_{10}H_{16}O_2$, m. p. 62—63°; terebic acid, $C_7H_{10}O_4$, m. p. 173—174°; and dipentene dihydriodide, $C_{10}H_{18}I_2$, m. p. 80°); (6) geraniol (diphenylurethane, m. p. 81—82°, and citral); (7) methyleugenol (bromomethyleugenol dibromide, $C_6H_2Br(OCH_3)_2 \cdot C_3H_5Br_2$, m. p. 78—79°; it is also shown that methylisoeugenol does not exist in the oil); (8) a blue oil, boiling above 260°, and consisting of oxygenated compounds of undetermined composition but of alcoholic nature; (9) a lactone, $C_{14}H_{20}O_2$, having a very aromatic odour, but present in the oil in very small amount; (10) palmitic acid; (11) acetic acid; (12) a mixture of fatty acids, $C_6H_{12}O_2$ to $C_{12}H_{24}O_2$. The acetic acid is contained in the oil in the form of esters, whilst the higher fatty acids are in a free state.

A quantitative determination of the principal constituents was made. The amount of methyleugenol, determined by Zeisel's method, was found to be 36·9 per cent. The amount of esters, calculated as $C_{10}H_{17} \cdot C_2H_3O_2$, is 27·5 per cent.; the free alcohols, $C_{10}H_{18}O$, 13·3 per cent. The amount of pinene obtained by direct fractionation of the oil was about 2 per cent., and the amount of high boiling constituents, such as the blue oil, is therefore about 20 per cent.

Discussion.

The President inquired as to the difference between *Asarum* and *Serpentaria*, the *A. Canadense* being known as Canada snake-root, whereas serpentaria was called Virginia snake-root.

Mr. Davis pointed out that Kremers had recently shown (*Pharm. Review*, 1901, 19, 200) that the dark colour of the oil of wild bergamot (*Monarda fistulosa*) is due to small quantities of thymoquinhydrone formed by oxidation from thymoquinol, and asked whether the dark blue colour of the higher boiling point fractions of the oil obtained by the authors might not be caused by the presence of a quinhydrone.

Dr. Power replied that although both *Asarum* and *Serpentaria* belong to the *Aristolochiaceæ*, they are very different, as are also the essential oils obtained from them. The oil from *A. Europæum* differs from that from *A. Canadense* in that the former contains the crystalline substance asarone, but apparently none of the alcohols or esters which are present in the latter. With regard to the colour of the oil, the chemical change noted by Kremers in oil of monarda would account for the red or brown colour of certain oils, but the colour of the blue oils must be attributed to substances of a totally different character.

155. "On the oxidation of sulphurous acid to dithionic acid by metallic oxides." By H. C. H. Carpenter.

Only two metallic oxides have hitherto been found to react with sulphurous acid so as to produce dithionic acid. These oxides are manganese dioxide and hydrated ferric oxide.

The object of the present research was the investigation of reactions which lead to the formation of dithionic acid, particular care being taken as to the purity of the sulphurous acid and the various oxides used. Dithionic acid is obtained when sulphurous acid reacts with (*a*) hydrated ferric oxide, $Fe_2O_3,3H_2O$, entirely freed from manganese; (*b*) hydrated manganic oxide, Mn_2O_3,H_2O, and (*c*) hydrated cobaltic oxide, $Co_2O_3,3H_2O$, but not with hydrated nickelic oxide, $Ni_2O_3,3H_2O$.

With hydrated ferric oxide, an almost theoretical yield of dithionic acid is obtained. Although it has not been found possible to obtain the theoretical yield of this acid from the corresponding hydrated oxides of manganese, cobalt, or nickel, yet there is very strong reason for believing, on account of the greater development of energy in the reduction of these oxides, that a partial or even complete decomposition of dithionic acid into sulphuric and sulphurous acids would take place. The facts which point to this conclusion are contained in the two following tables. The first shows the percentages of dithionic and sulphuric acids obtained from the four hydrated oxides already mentioned; the second indicates the changes of energy, expressed in thermal units, involved in the reduction of the oxides.

I.

Hydrated Oxides.	Percentage dithionate.	Percentage sulphate.
Ferric	96·06; 96·23	Not estimated
Manganic	75·52; 74·53	25·42
Cobaltic.....	36·97; 35·07	63·80; 63·33
Nickelic.....	Nil	101·04

II.

Reduction of the hydrated oxides.	Heat of reaction.
$Fe_2(OH)_6 = 2Fe(OH)_2 + O + H_2O$.....	−546 K
$Mn_2(OH)_6 = 2Mn(OH)_2 + O + H_2O$.....	−448 K
$Co_2(OH)_6 = 2Co(OH)_2 + O + H_2O$.....	−225 K
$Ni_2(OH)_6 = 2Ni(OH)_2 + O + H_2O$.....	+13 K

A comparison of the two tables shows that the greater the energy required for the reduction of the hydrated oxides, the larger is the

percentage yield of dithionic acid. The maximum yield is obtained with ferric hydrate, where the energy that needs to be supplied is such that it is possible to stop the reaction almost wholly at the stage represented by the equation (i), $Fe_2(OH)_6 + 3SO_2 = FeS_2O_6 + FeSO_3 + 3H_2O$.

Whether the slight deficit from the theoretical number is due to a slight decomposition of the nature (ii), $FeS_2O_6 = FeSO_4 + SO_2$, or to a defect in the method of estimation used, is a question which it has not been found possible to decide.

In the case of manganic oxide, about one-quarter, and in the case of cobaltic oxide, about two-thirds, of the dithionic acid formed is decomposed in the manner indicated in equation (ii).

The reduction of nickelic oxide differs essentially from that of the other three in being an exothermic change, and the energy liberated is such that the reaction cannot be stopped at the intermediate stage, but proceeds wholly to the last stage, and the only oxidation product is sulphuric acid.

The author has confirmed the results of Gay-Lussac and Welter, who showed that no dithionic acid was obtained by the reduction of the peroxides of lead and barium with sulphurous acid. In view of the negative character of these results, the action of sulphurous acid on the dithionates of these metals was studied. It was found that solutions of barium dithionate are quite unaltered, except at a temperature at which the influence of heat alone begins to be seen, when a gradual decomposition into barium sulphate and sulphur dioxide sets in. On the other hand, solutions of lead dithionate are decomposed instantaneously, even at 5°, lead sulphite being precipitated and free dithionic acid remaining dissolved.

156. "Optically active β-hydroxybutyric acids. Preliminary note." By A. McKenzie.

For certain work the author has been desirous of obtaining *d*- and *l*-β-hydroxybutyric acids. That a substance so simply constituted as externally compensated β-hydroxybutyric acid has not before this been resolved into its optically active components is due to the fact that the salts formed by neutralisation with the common alkaloids are readily soluble and crystallise with some difficulty. The author has resolved the inactive acid, which was prepared by the reduction of acetoacetic ester by sodium amalgam, by means of quinine with water as solvent. After systematic crystallisation, the neutral *l*-acid-*l*-quinine salt was isolated. This salt, which crystallises well, contains $4\frac{1}{2}H_2O$, is very

easily soluble in cold ethyl alcohol, moderately so in chloroform, sparingly so in benzene, acetone, carbon tetrachloride, and in ether, and easily in boiling ethyl acetate. An alcoholic solution of the air-dried salt had the rotation $[\alpha]_D^{15°} = -129{\cdot}9°$ ($c = 2{\cdot}814$). The anhydrous salt melted at 124·5—125·5°. The *l*-acid from the quinine salt gave $[\alpha]_D^{15°} = -24{\cdot}9°$ ($c = 8{\cdot}3304$), whilst the sodium salt prepared from it gave $[\alpha]_D^{15°} = -14{\cdot}5°$ ($c = 8{\cdot}518$). These values for the specific rotations of the acid and its sodium salt agree with the values of Magnus-Levy, who obtained the *l*-acid from diabetic urine (*Archiv. für experim. Path. und Pharmak.*, 1901, 45, 389).

The author prepared some *l*-acid from diabetic urine by the method of Magnus-Levy and converted it into quinine salt. The product, when deprived of its water of crystallisation, melted at 124·5—125·5°; an alcoholic solution of the air-dried salt gave $[\alpha]_D^{15°} = -129{\cdot}0°$ ($c = 2{\cdot}8052$).

Experiments are in progress with the object of isolating the *d*-acid by means of strychnine, the *d*-acid-*l*-strychnine salt being more insoluble in water than the *l*-acid-*l*-strychnine salt.

157. "Note on the reduction of trinitrobenzene and trinitrotoluene with hydrogen sulphide." By J. B. Cohen and H. D. Dakin.

By the reduction of 1 : 3 : 5-trinitrobenzene and 2 : 4 : 6-trinitrotoluene in alcoholic solution with hydrogen sulphide in presence of a trace of ammonia, the corresponding dinitrohydroxylamine compounds are formed, $C_6H_3(NO_2)_3 + 2H_2O = C_6H_3(NO_2)_2NHOH + H_2O$. *Dinitrophenylhydroxylamine* is an orange, crystalline substance, m. p. 114—116°, soluble in alcohol, benzene, and in hot dilute hydrochloric acid; *dinitrotolylhydroxylamine* crystallises from benzene in yellow rhombohedral crystals and from dilute hydrochloric acid in needles, m. p. 143—145°. Both compounds reduce alcoholic silver nitrate and Fehling's solution; they are slowly decomposed on boiling with dilute, more rapidly with concentrated hydrochloric acid, yielding the amido-compounds and losing oxygen, $C_6H_3(NO_2)_2NHOH = C_6H_3(NO_2)_2NH_2 + O$. In the case of trinitrotoluene, the nitro-group in the ortho-position undergoes reduction, a curious fact, seeing that ammonium sulphide effects the reduction of the para-nitro-group. The 2 : 4-dinitro-6-toluidine, obtained by the action of strong hydrochloric acid on dinitrotolylhydroxylamine, is a colourless substance crystallising in needles and melting at 212—213°.

158. "The synthesis of alkyl-substituted tricarballylic acids." By W. A. Bone and C. H. G. Sprankling.

The authors have investigated two methods for the preparation of ethyl cyanotricarballylates from succinic acids, as follows: (1) By the interaction of the sodium compounds of ethyl cyanosuccinates with the esters of α-bromo-fatty acids, as indicated by the general equation (where R = hydrogen or an alkyl group)

$$CR_2Br(CO_2Et) + NaC(CN)(CO_2Et)\cdot CR_2(CO_2Et) = CR_2(CO_2Et)\cdot C(CN)(CO_2Et)\cdot CR_2(CO_2Et) + NaBr,$$

and (2) by the interaction of ethyl monobromosuccinates with ethyl sodiocyanacetate, according to the equation

$$CR_2(CO_2Et)\cdot CRBr(CO_2Et) + NaCH(CN)(CO_2Et) = NaBr + CR_2(CO_2Et)\cdot CR(CO_2Et)\cdot CH(CN)(CO_2Et).$$

They find that whilst the first method is quite a general one and affords good yields of ethylcyanotricarballylates, the second has a more limited application (mainly on account of the tendency which ethyl bromosuccinates exhibit to lose hydrogen bromide and form unsaturated esters), and even in cases where it can be applied, the yields are not so good as those obtained by the first method. The properties of tricarballylic acid itself and a number of alkyl-substituted acids of the series, their anhydro-acids, and monomethyl salts have been studied. Some of these are indicated in the following table:

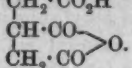
Acid.		M. p.	Dissociation constant.	M. p. of anhydro-acid.
Tricarballylic		157—159°	0·022	130—131°
α-Methyltricarballylic	(1)	179	0·0322	liquid
	(2)	134—135	0·0480	liquid
$\alpha\alpha_1$-Dimethyltricarballylic	(1)	206—207	0·0450	110—112
	(2)	174	0·0545	130
	(3)	143	0·0572	116—117
αα-Dimethyltricarballylic		143	0·0318	135—136
$\alpha\alpha_1$-Di*iso*propylic	(1)	173	0·1930	liquid
	(2)	156	0·1625	liquid

Monomethyl salts of tricarballylic and αα-dimethyltricarballylic acids have been prepared by three methods, namely, (1) direct partial esterification of the acids, (2) partial hydrolysis of trimethyl salts, (3) the solution of anhydro-acids in methyl alcohol. The products are liquid, but a study of their dissociation constants shows that each of the three methods indicated yields a *single* monomethyl salt, and not a

mixture of isomeric monomethyl salts. The dissociation constants of these salts are as follows:

Acid.	Monomethylic salts by		
	Direct esterification of acid.	Partial hydrolysis of trimethylic salt.	Solution of anhydro-acid in CH_3OH.
Tricarballylic	0·0075	0·00925	0·00945
αα-Dimethyltricarballylic ...	0·0180	0·00865	0·0186

Since the monomethyl salts obtained by direct esterification of the acids most probably have the formulæ $CH_2(CO_2H)\cdot CH(CO_2H)\cdot CH_2(CO_2Me)$ and $(CH_3)_2C(CO_2H)\cdot CH(CO_2H)\cdot CH_2(CO_2Me)$ respectively (because a carboxyl attached to a *primary* carbon atom is always more readily esterified than one attached to a secondary or tertiary carbon), it follows that the monomethyl tricarballylate obtained by partial hydrolysis of the trimethyl salt, and by solution of the anhydro-acid in methyl alcohol, must have the formula $CH_2(CO_2H)\cdot CH(CO_2Me)\cdot CH_2(CO_2H)$, and therefore that the constitution of the anhydro-acid must be represented thus,



159. "Note on the constitution of limettin." By W. A. Tilden and H. Burrows.

In a previous communication (Tilden, *Trans.*, 1892, **61**, 344), it was shown that limettin, $C_{11}H_{10}O_4$, had the following composition: $C_6H_3\langle{}^{(OCH_3)_2}_{C_3HO_2}$.

Further experiments have been undertaken, with the object of determining the structure of the group C_3HO_2.

In the meantime, the publication of a communication by E. Schmidt (*Apoth. Zeit.*, 1901, 71, 619) on a substance which he has isolated from oil of lemon and has identified with limettin, and the appearance of a recent note by Burgess (this vol., p. 171) render it necessary to place on record the following results, although at present incomplete.

The dibromo-compound previously described by Tilden (*loc. cit.*) melts at 297° with decomposition, and not at 257°.

On treatment with 10 per cent. solution of potash, it yields an acid of the composition $C_{11}H_9O_5Br$. Continued treatment with potash does not remove the second atom of bromine.

It is therefore highly probable that the structure of the group C_3HO_2 is similar to that of the ring in coumarin, dibromocoumarin behaving in exactly the same way. Dibromolimettin may therefore be represented as $(CH_3O)_2{\cdot}C_6HBr\langle{}^{CH:CBr}_{O-CO}$.

When treated with potash, dibromolimettin gives the corresponding *coumarilic acid*, $(CH_3O)_2C_6HBr\langle{}^{CH}_{O}\rangle C{\cdot}CO_2H$, from the *potassium* salt of which the *methyl ester* was prepared (m. p. 181°).

On subjecting dibromolimettin to further action of bromine in a sealed tube, a *tribromo*-derivative was prepared containing two hydroxyl groups; the corresponding *diacetyl* compound melts at 244°.

The following chlorine compounds have been prepared:

Monochlorolimettin, which melts at 242° and is not acted upon by solutions of alkaline hydroxides. *Dichlorolimettin* melts at 275° and, like the dibromo-compound, with potash gives *monochlorocoumarilic acid*. The trichloro-derivative prepared by Tilden (*loc. cit.*) similarly gives *dichlorocoumarilic acid*.

When limettin is heated on the water-bath with a solution of sodium ethoxide, the *sodium* salt is quickly deposited. Attempts to prepare the methyl derivative were unsuccessful, but when the *silver* salt was heated with a solution of methyl iodide in methyl alcohol, a substance which crystallised in white tufts of needles (m. p. 189°) was isolated, together with re-formed limettin. Analyses showed the substance to have the formula $C_{12}H_{12}O_4$, differing from limettin by CH_2. Its chemical properties are similar to those of limettin, as it readily forms a *bromo*-derivative and a coumarilic acid.

160. "Derivatives of β-bromocamphor." By H. E. Armstrong and T. M. Lowry, D.Sc.

By heating ordinary *aa'*-dibromocamphor with hydrogen bromide under certain conditions, it is converted into an isomeric *aβ*-compound, one of the bromine atoms being transferred from the lateral CBr_2 group. Kachler and Spitzer have shown that this *aβ*-dibromocamphor is converted by nitric acid into an *aβ*-dibromonitrocamphor. The authors find that a *β*-bromocamphoric acid is also produced, isomeric with the acids described by Wreden and by Kipping and Pope. The close resemblance between this *β*-acid and the isomeric *π*-acid suggests that the two compounds are similar in constitution—perhaps stereoisomerides: in other words, that the bromine is present in one of the median methyl groups in the $-CMe_2-$ group of the camphor molecule.

β-Bromocamphoric acid, $C_8H_{12}Br(CO_2H)_2$, softens at about 205° and melts at 208—210°, gas being liberated; in a 5 per cent. solution in

alcohol at 10°, $[\alpha]_D = +39{\cdot}7°$. The corresponding *anhydride*, $C_8H_{13}Br\langle{CO \atop CO}\rangle O$, crystallises from dilute acetone in long, glistening needles; it melts at 142°; in a 4 per cent. solution in acetone at 10°, $[\alpha]_D = -2{\cdot}8°$.

β-Bromonitrocamphor, $C_8H_{13}Br\langle{CH\cdot NO_2 \atop CO}$, prepared by reducing *αβ*-dibromonitrocamphor, crystallises from alcohol in short prisms; when heated, it softens at 100° and melts at 112°, but after fusion and solidification remelts sharply at 100°; being a secondary nitro-compound, it forms salts; and freshly-prepared solutions exhibit the phenomena of mutarotation.

A third product of the action of nitric acid on *αβ*-dibromocamphor is a *tribromocamphor*, $C_{10}H_{13}Br_3O$, which melts at 66°; in a 2·5 per cent. solution in acetone, $[\alpha]_D = +2°$; it separates in a crystalline form on reducing the crude crystalline dibromonitrocamphor, and appears to be identical with the compound obtained by de la Royère by heating *αβ*-dibromocamphor with phosphorus pentabromide (*Bull. Soc. Chim.*, 1882, **38**, 580).

β-Bromo-derivatives of camphor are also obtained on decomposing by heat the sulphobromides derived from the "Reychler" series of acids (Armstrong and Lowry, this vol., p. 182): *e.g.* *α*-bromocamphor-*α'*-sulphobromide, $C_8H_{14}\langle{CBr\cdot SO_2Br \atop CO}$, when decomposed in this way, gives *αβ*-dibromocamphor, $C_8H_{13}Br\langle{CHBr \atop CO}$; *α*-chlorocamphor-*α'*-sulphobromide, $C_8H_{14}\langle{CCl\cdot SO_2Br \atop CO}$, gives *α*-chloro-*β*-bromocamphor, $C_8H_{13}Br\langle{CHCl \atop CO}$, the products obtained being identical with those formed by heating *α*-bromocamphor and *α*-chlorocamphor with bromine in sealed tubes.

ADDITIONS TO THE LIBRARY.

I. By Donation.

Hjelt, Edoard, Aschan, Ossian, Cohnheim, O., Emmerling, O., und Vahlen, E. Roscoe-Schorlemmer's ausführliches Lehrbuch der Chemie von Jul. Wilh. Brühl. Neunter Band. Braunschweig. 1901.
From the Publishers.

II. By Purchase.

Buchner, Georg. Die Metallfärbung und deren Ausführung, mit besonderer Berücksichtigung der chemischen Metallfärbung. Zweite, verbesserte, und vermehrte Auflage. Berlin. 1901.

Lindner, Paul. Mikroskopische Betriebskontrolle in den Gärungsgewerben mit einer Einführung in die technische Biologie, Hefenreinkultur, und Infektionslehre. Dritte, neubearbeitete Auflage. Ill. Berlin. 1901.

Lorenz, Richard. Elektrochemisches Praktikum. Ill. Gottingen. 1901.

van Rijn, J. J. L. Die Glykoside: chemische Monographie der Pflänzenglykoside nebst systematischer Darstellung der künstlichen Glykoside. Berlin. 1901.

Schultz, Gustav. Die Chemie des Steinkohlentheers. Dritte vollständig umgearbeitete Auflage. Zweiter Band: die Farbstoffe. Ill. Braunschweig, 1901.

Witt, Otto N. Die chemische Industrie auf der internationalen Weltausstellung zu Paris 1900. Berlin. 1902.

Pamphlets.

Imperial Department of Agriculture for the West Indies. Report on certain economic experiments conducted in connection with the Botanic Station, Antigua, 1900—1901. Barbados. 1901.

Imperial Department of Agriculture for the West Indies. Sugar-cane experiments in the Leeward Islands. Report on experiments conducted at Antigua and St. Kitts in the season 1900—1901. Part I. Experiments with varieties of sugar-cane, with an appendix on the chemical selection of sugar-cane. Part II. Manurial experiments. Barbados. 1901. From C. H. G. Sprankling.

Dymond, T. S., and F. Hughes. Notes on agricultural analyses made in the County Technical Laboratories, Chelmsford, during the years 1896—1901. From the Authors.

Patent Office. Subject list of works on certain chemical industries, including destructive distillation, mineral oils and waxes, gas lighting, acetylene, oils, fats, soaps, candles, and perfumery, paints, varnishes, gums, resins, paper and leather industries, in the Library of the Patent Office. From the Comptroller-General of Patents.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before December 9th.

LIBRARY CATALOGUE.

A new Catalogue of the Library, arranged under authors' names and subjects in accordance with the system adopted in indexing the Society's publications, is ready for the press. Fellows who desire a copy of the Catalogue, at a cost of 2*s.* 6*d.*, are requested to send in their names to the Secretaries not later than January 31st, 1902.

If a sufficient number of names is not received, the catalogue will not be printed.

MEMORIAL LECTURES, 1893—1900.

Fellows can now obtain copies of the volume of collected Memorial Lectures on application to the Assistant Secretary, price 7*s.* 6*d.* post free.

At the next meeting, on Thursday, December 5th, there will be a ballot for the election of Fellows, and the following papers will be communicated:

"Influence of substitution on the formation of diazoamines and aminoazo-compounds." By G. T. Morgan.

"The determination of available plant food in soils by the use of dilute solvents." By A. D. Hall and F. J. Plymen.

"Some new derivatives of gallic acid." By F. B. Power and F. Shedden.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, December 5th, 1901.

Allen, Frederick Thomas,
15, Sea View Terrace, Hartlepool.

Teacher. For two years student at Wellingborough Technical School. Three years at Durham College of Science, Newcastle-upon-Tyne. Bachelor of Science, Durham University.

P. Phillips Bedson.	C. H. Creasey.
F. C. Garrett.	*S. Hoare Collins.*
J. W. Patterson.	*Beeby Thompson.*

Baker, Arthur,
130, Walmersley Road, Bury, Lancs.

Works' Chemist (Paper Mill). Desirous of obtaining the Journal and keeping in touch with chemical progress. Three years' study of Advanced Chemistry and Physics at the Bury Grammar School. Attended Evening Courses in Advanced Chemistry at the Bury Technical School under W. Dixon, Esq. Silver Medallist and First Class Honours, with First Prize, in the Paper Manufacture Exam., under City and Guilds, 1901. Assisted W. French, M.A., in his private work. Two and a half years Chemist at Woolfold Paper Mill, Bury.

William French.	William Dixon.
W. M. Brothers.	Jul. Hübner.

Jas. Grant.

Baker, Thomas Thorne,
28, Church Road, Forest Hill, S.E.

At present studying for B.Sc., and carrying out research in connection with photo-decomposition. Have contributed articles on sen-

sitive compounds to most of the photographic papers. Carried out research in connection with electro-chemical nature of the latent image in photo-decomposition, and read papers at some of the London Societies on the subject. Have laboratory at home specially adapted to and fitted out for this purpose. Investigated and written about the sensitive uranyl compounds, also the sensitive molybdic and tungstic salts, and their decomposition products. Am F.R.P.S., and have passed Inter. B.Sc. (Lond.).

Charles M. Stuart.	Thomas Bolas.
S. Barlet.	J. W. Shepherd.

Chapman Jones.

Ball, Walter Craven,

Trinity College, Oxford. Present Address, 19, Lewisham Hill, Lewisham, S. E.

Scholar of Trinity College, Oxford. Late Demonstrator of Chemistry, Balliol College Laboratory, Oxford. Demonstrator in Chemistry, Guy's Hospital, London. First Class Honours in Chemistry, Oxford, 1899.

[John Conroy.]	William E. Moss.
John Wade.	Walter C. C. Pakes.
D. H. Nagel.	Thos. Stevenson.

A. Vernon Harcourt.

Bennet, Andrew Russell,

1, Wildman Street, Nottingham.

Pharmaceutical Chemist. Principal of the Nottingham School of Pharmacy. Author of a "Report on Commercial Ginger, with suggestions for a Pharmacopœial Standard."

Geo. Clayton.	*Jas. Baynes.*
Edwd. Francis.	*F. Stanley Kipping.*
Harold B. Holthouse.	*R. M. Caven.*
Thos. Stevenson.	*G. D. Lander.*

Bickford, Harding,

46, Currie Street, Adelaide, S. Australia.

Manufacturing Chemist. Have studied Chemistry in Australia, and subsequently three years' analytical work at the South London Central Public Laboratory.

John Muter.	Will. F. Mawer.
James W. Epps.	*John C. Umney.*
A. H. M. Muter.	*Fred. W. Fletcher.*

Boyers, Henry,

20, Knox's Street, Sligo.

Manufacturing Chemist. Member of the Pharmaceutical Society of Ireland since 1889, by Examination. Studied Chemistry at Carmichael College, Dublin, under Professor Lapper, for two years. Am interested in Chemical Science, specially as applied to Agriculture, and am desirous of obtaining the publications of the Society.

Thomas Tyrer.	*Chas. R. C. Tichborne.*
Thomas Morson.	*Isaac S. Scarf.*
Harold W. Harrie.	*E. J. Jackman.*

Burton, William.

Cotleigh, Nunnery Fields, Canterbury.

Assistant Master, Simon Langton Schools, Canterbury. Bachelor of Science (Hons. in Chem.), Univ. of Wales, also Hons. in Chem. at Inter. Science (Lond.). Student-assistant in Chem. Laboratory of University College of Wales, Aberystwyth. Science Master in Neuenheim College, Heidelberg; and afterwards at Denstone College, Staffordshire. Now Assistant Master in School of Science at Simon Langton School, Canterbury.

H. Lloyd Snape.	Edward J. Russell.
James J. Dobbie.	*A. D. Hall.*
Humphrey O. Jones.	*John Percival.*

Cormack, William.

3, Westfield Place, Eskbank, Midlothian.

Chemist at Messrs. Annandale and Sons, Ltd., Polton Paper Works, Midlothian. Worked five years in Chemical Laboratory, University College, Dundee. Published (*a*) Apparatus for Steam-distillation (*Chem. News*, **75**, 289); (*b*) Estimation of Furfuraldehyde (*Jour. Chem. Soc.*, **77**, 990); jointly with Professor Walker: (*c*) Dissociation-constants of Weak Acids (*Jour. Chem. Soc.*, **77**, 5); (*d*) Campholytic and Isolauronolic Acids (*Jour. Chem. Soc.*, **77**, 374).

James Walker.	John H. Wigner.
John S. Lumsden.	John Foggie.

Leonard Dobbin.

Crookes, Samuel Irwin,

Thanet Street, Clay Cross, Chesterfield.

Senior Science Master, District Secondary School, Clay Cross. Pursuing the study of Chemistry in spare time at the University College, Sheffield.

W. Carleton Williams.	T. Slater Price.
George Young.	E. Witham.

William H. Oates.

Crossley, Frank,

Duchy Bank, Seedley Road, Pendleton, Manchester.

Analytical Chemist. For four years assistant to J. Carter Bell, Esq., Analyst to the County of Chester, and Boroughs of Salford, Birkenhead &c. Afterwards, during the arsenic scare in Beer, with Dr. Miller (Analyst to Brewers' Association). Since on my own account in analytical work.

J. Carter Bell. — Frank Scudder.
Alex. K. Miller. — Francis Jones.
C. Estcourt.

Davidson, John Howard,

Goldenhill, Stoke-on-Trent.

Managing Chemist to Mr. J. H. Williamson, Goldenhill Colour Works. For three years student in the Owens College Chemical Department. B.Sc. with Honours in Chemistry (Victoria), 1899. Research Student, 1899–1900.

Harold B. Dixon. — Wm. A. Bone.
D. L. Chapman. — W. H. Perkin, jun.
W. T. Lawrence.

Davis, Francis,

Whitwell, Elland, Yorks.

Director of "The Yorkshire Indigo, Scarlet, and Colour Dyers, Limited." Passed full course in Chemistry in classes connected with South Kensington. Obtained first prize Elementary, 1876, first prize Advanced, 1877, first prize Honours, 1880, in Wool-Dyeing, Soc. of Arts, and City and Guilds of Lond. Inst. Author of prize essay on "Best Chemical Methods of Treating the Waste Products in Woollen Manufacture," Cloth Workers', 1879. Author of prize essay on "Logwood, its Practical and Chemical Treatment," Cloth Workers', 1881; and take an interest in chemical progress generally.

William Ackroyd. — *J. K. Crow.*
Thomas J. Underhill. — *Colin Gordon.*
Leonard P. Wilson. — *B. S. Bull.*

English, Robert,

8, Colwall Villas, Burley Road, Beckenham, Kent.

Chief Chemist Crystal Palace District Gas Co., Lower Sydenham, S.E. Chief Chemist Crystal Palace D. Gas Co., two and a half years. Gas Examiner Gas Light and Coke Co., Beckton, seven years.

Samuel Rideal. — W. W. Duffield.
Vivian B. Lewes. — *F. Napier Sutton.*
H. F. Hills. — *Walter Grafton.*

Gadd, Henry Wippell,
42, Union Road, Exeter.
Analytical Chemist.

Wyndham R. Dunstan. Thos. Tyrer.
John Attfield. Arthur W. Clayden.
Benj. H. Paul.

Gillman, Edward,
Barbados, West Indies.

Chief Assistant Government Laboratory, Barbados. Analyst (Agricultural Chemistry, Sugar Chemistry, Foods and Drugs): has assisted during the past nine years in Agricultural research connected with sugar cultivation, official reports of which are published by the Barbados Government.

J. P. d'Albuquerque. John R. Bovell.
H. H. Cousins. *J. B. Harrison.*
Jno. Williams.

Groves, William Peer,
Oldfield Hall, Altrincham, Manchester.

Graduate of Cambridge University, Christ's College. B.A. with Honours in Science (Chemistry, Zoology, Botany, &c.). Two months with Dr. Miller, Ph.D., F.I.C., &c. (Manchester), during the recent "Arsenic scare." Pupil and occasional Demonstrator at Rossall School, Lancs.

Fred. R. Stone. W. B. Roberts.
Alex. K. Miller. *J. Jackson.*
J. M. Collett.

Hammond, Herbert Blackmore,
3, Vicar's Close, Lichfield, Staffs.

Assistant Brewer and Chemist to Messrs. The Lichfield Brewery Co. Ltd. Two years general chemistry, inorganic and organic, under the tuition of Mr. J. M. Murray, M.Sc., F.C.S. Private work on the analysis of foodstuffs for experience. Course of brewing chemistry under Mr. A. C. Chapman, F.I.C., F.C.S. Two years in the above position.

Alfred C. Chapman. J. Moore Murray.
Henry P. Harris. *Arthur Hartley.*
Lawrence Briant.

Harding, Herbert,
20, Stratford Road, Kensington, W.

Chemical Student. I studied chemistry for three years at Finsbury Technical College, obtaining the College Certificate, and since October, 1900, have been working under Prof. Armstrong at the Central Technical College.

Henry E. Armstrong. Gerald T. Moody.
R. Meldola. William A. Davis.
T. Martin Lowry.

Hermann, Charles Thomas Gardner,
London Hospital, E.

Chemist (Pharmaceutical). Formerly Lecturer on Chemistry, Lonsbury College, Clapton. General Interest in Chemistry and anxious to have the Society's Journal.

Frederic Jas. M. Page. John R. Brooke.
Hugh Candy. *P. Gerald Sanford.*
W. C. Young.

Hobson, Edwin,
3, Oxford Road, Liscard, Cheshire.

Analytical Chemist. Formerly student at City of London College and City Guilds Technical College. Assistant to Messrs. Cannon and Newton, 39, Mincing Lane, E.C. For the past nine years chemist and manager of the Phospho-Guano Company, Ltd., Seacombe, Cheshire.

William Newton. P. Gerald Sanford.
J. Owen Alexander. *D. G. Riddick.*
Reg. T. Marshall. *Jas. Baynes.*

Ingram, Beresford,
19, Lewisham Hill, Lewisham, S.E.

Science Master at Colfe's Gram. Sch. Science Tripos, 1900, Cambridge. Teaching Analytical Chemistry at above School. I desire to have access to the Library of the Society.

R. H. Adie. Francis Jones.
K. C. Browning. R. L. Taylor.
Edmund M. Rich.

Johnson, Charles Harold, M.B., Ch.M., F.R.C.S.E., D.P.H.,
"Beaumont," Northcote, Melbourne, Victoria, Australia.

Medical Practitioner. Diploma in Public Health (after six months' working in a chemical laboratory, at Lindsay Place). My reason for desiring Fellowship is to keep in touch with Chemistry on this side of

the world. I am expecting an appointment in Public Health in Melbourne on my return.

G. H. Gemmell.	*W. Ivison Macadam.*
Alex. Crum Brown.	*J. Falconer King.*
Leonard Dobbin.	*R. R. Tatlock.*
Hugh Marshall.	*R. T. Thomson.*

Jollyman, Walter Henry,

Spartan House, Colney Hatch Lane, Muswell Hill, N.

Analyst to the Laboratory of Clinical Pathology. Three years student at Technical College, Finsbury. Assoc. Inst. of Chemistry. For two years Research Assistant to Dr. W. C. C. Pakes, F.C.S., &c. Jointly in Chemical Society's Journal, "The Collection and Examination of the Gases produced by Bacteria," "The Bacterial Decomposition of Formic Acid," "The Bacterial Oxidation of Formates by Nitrates."

Thos. Stevenson.	Walter C. C. Pakes.
John Wade.	Norman Leonard.

Otto Hehner.

Kettle, James David, B.Sc. (Lond.),

1, Vardens Road, St. John's Hill, S.W.

Chemist to the Rubber Chemical Co., Seringa Mills, Mitcham. Student at the Battersea Polytechnic for four years, at first under Dr. Bone, and later under Mr. Wilson. Assistant in Works Analytical Laboratory for four years.

William A. Bone.	Thomas Tyrer.
John Wilson.	J. W. Shepherd.
C. Edward Sage.	John Barclay.
John McArthur.	*Willie Briggs.*

Bruce-Kingsmill, Julian,

Ordnance College, Woolwich.

Captain in the Royal Regiment of Artillery (presently engaged in the Chemical Laboratory, Ordnance College, Woolwich). Certificate in Qualitative Analysis, University of Berlin. Honours in Chemistry, Intermediate Education Board, Ireland. Diploma (as Associate) Glasgow and West of Scotland Technical College. University of Glasgow, three sessions' work in Qualitative and Quantitative Analysis, including the Chemistry of Organic Compounds. Analysis of Beer; Chemistry of Explosives; Investigation of some rarer Coal Tar Products; Investigation of some Properties of Liquefied Air; Paper on "Coal Samples from the Lanarkshire Collieries."

Passed M.A. Examination in Chemistry, University of Glasgow,
Passed C.E. „ „ „ „
Passed B.Sc. „ „ (Honours) „ „ 1898.
Member of the Institution of Engineers and Shipbuilders of Scotland.
Life Member Glasgow University Engineering Society, &c.

F. Nolan Baker.	W. R. Hodgkinson.
Gerald T. Moody.	*Bernard F. Howard.*
William A. Davis.	*R. Meldola.*
William A. Lethbridge.	*F. Southerden.*

Larter, Alfred Tabois,
184, Holland Park Avenue, W.
Student of Chemistry. Studied two years at the Finsbury Technical College, and two years at the Central Technical College, obtaining the Diploma of Associate of the City and Guilds Institute.

Henry E. Armstrong.	T. Martin Lowry.
Gerald T. Moody.	William A. Davis.

James Moir.

Macdonald, Peter,
Lapstone Road, Millom, Cumberland.
Analytical Chemist. Six years as student and assistant in laboratory of Messrs. Tatlock and Thomson, City Analysts, Glasgow, and two years Chemist to Millom Iron Works, Millom.

R. R. Tatlock.	Jas. D. Dougall.
R. T. Thomson.	T. K. Cockburn.

Horatio Ballantyne.

Millard, Charles Killick,
The Gilroes, Groby Road, Leicester.
Medical man. Doctor of Medicine and Doctor of Science (Edinburgh). Public Analyst for Leicester.

Alfred Hill.	Jas. O'Sullivan.
C. O'Sullivan.	Chas. Geo. Matthews.

Arthur L. Stern.

Miller, Edward Holl,
Common Hall, Hadleigh, Essex.
Student at Technical College, Finsbury.

Raphael Meldola.	F. Southerden.
Chas. R. Darling.	Bernard F. Howard.

J. Vargas Eyre.

Müller, Christian,
10, Selwyn Avenue, Richmond, Surrey.
Tutor. Studied Chemistry, Physics, and Botany at a German "Realschule" and University of Giessen. Am interested in the

Chemistry of Vegetable Physiology, and should find the Society's publications of much use. Wish, by attending the meetings and reading the Journal, to keep myself acquainted with current chemical research, here and in other countries.

Watson Smith. Oscar Guttmann.
E. G. Clayton. *Percy A. E. Richards.*
A. Percy Hoskins.

Newbould, Herbert Simpson,
Trinity Hall, Cambridge.
Undergraduate. First Class, Natural Science Tripos, 1901, Part I.

S. Ruhemann. M. M. Pattison Muir.
R. S. Morrell. *R. H. Adie.*
R. M. Caven.

Parkes, Albert Edward,
Borough Analyst's Office, 43 Whitehorse Street, Stepney, E.
Analyst to the Stepney Borough Council. For three years student at Mason College, Birmingham. For two years Chief Assistant to T. V. Hughes, Esq., F.I.C., F.C.S. For one-and-a-half years Chief Assistant to J. Kear Colwell, Esq., F.I.C., F.C.S. Fellow of the Institute of Chemistry. Member of the Society of Chemical Industry.

J. Kear Colwell. T. Slater Price.
Harry Silvester. A. Lapworth.
Percy F. Frankland. *Arthur R. Ling.*

Pollitt, Charles James Tomlin,
"Athole," Church Street, Croydon, Sydney, N.S.W.
Analytical Chemist. Studied on Science Side, Manchester Grammar School. Three years articles with Mr. Chas. Estcourt, Manchester City Analyst; eighteen months Chief Assistant Mr. Estcourt. Two-and-a-half years London Laboratory, Rio Tinto Co. Last six years Chief Chemist Laboratory of Co-operative Wholesale Society. Now Managing Chemist of Australian Works of Co-operative Wholesale Society.

W. MacKean. P. Anderson Estcourt.
Percy Haigh. J. E. Green.
Henry Bailey.

Potter, Rowland Samuel,
2, Museum Hill, Haslemere, Surrey.
Research Chemist. Associate of City and Guilds of London Institute.

For two years chemist to a tar distillery (Major and Co., Hull). At present employed in photo-chemical research.

Henry E. Armstrong. Edward W. Lewis.
William A. Lethbridge. William A. Davis.
T. M. Lowry.

Royle, Charles Leonard,
Nellikuppam, South Arcot, India.

Chemist to Sugar Refinery. Formerly student at Finsbury Technical College. Chemist one year at Abram Lyle and Sons; four years David Martineau and Co.; two years Fowler Bros.; one year Glebe Sugar Refinery; five years, and now, Chemist to East India Sugar Factories and Distillery, Nellikuppam, South Arcot, India. Wishes to keep *au courant* with Chemical Science by means of the Journal of the Society.

B. E. R. Newlands. R. Meldola.
Thomas Royle. Thos. Tyrer.
Arthur R. Ling. *F. Southerden.*

Ryffel, John Henry,
10, Onslow Gardens, Highgate, N.

Chemistry Demonstrator at Guy's Hospital. B.A. Cambridge, 1899. First Class, Chemistry, Nat. Sci. Tripos, Pt. II., 1900. B.Sc. London, 1901, First Class, Chemistry. Assistant Demonstrator at the Cambridge University Chemical Laboratory, one year, 1900—1901.

G. D. Liveing. John Wade.
W. J. Sell. F. W. Dootson.
H. J. H. Fenton. W. H. Mills.
H. O. Jones.

Sandford, Allan,
Market Place, Ulverston.

Analyst and Sampler. Second Class Diploma in Chemistry, Barrow Higher Grade School. Ten years Barrow Hematite Iron and Steel Co. Laboratory. Two-and-a-half years Pyle and Blaina Works, Ltd., Blaina, R.S.O., Mon., Laboratory. Two-and-a-half years Isle of Elba, Italy.

James E. Ferguson. A. C. Aitken.
William M'Call. Robt. D. Connell.
Rd. Spencer.

Scott, George Charlton,
Eston Grange, Grangetown, R.S.O., Yorks.

Analytical Chemist. Advanced Stage, Science and Art Exams. First Class in Practical and Second Class in Theoretical Chemistry.

Seven years of Laboratory experience. To be in touch with the most recent discoveries and advancements of the Science.

J. Archyll Jones. J. E. Stead.
Fredk. Doyle. *C. H. Ridsdale.*
H. E. Wright.

Sherwood, Edward Charles,
39, Vincent Square, Westminster.

Senior Science Master, St. Peter's College, Westminster. Late Nat. Science Demy, Magdalen College, Oxford. 2nd Class Math. Moderations; 2nd Class Final Mathematics; 2nd Class Chemistry. Four years Science Master at Magdalen College School, Oxford; two terms Science Master at Westminster School.

John Watts. P. Elford.
J. E. Marsh. J. A. Gardner.
H. L. Bowman. W. W. Fisher.

Smith, Norman,
15, King Street, Bury.

Demonstrator and Assistant Lecturer in Chemistry, the Owens College, Manchester. B.Sc. with First Class Honours in Chemistry, Victoria University, 1898, after four years' study in the Owens College; Mercer Scholar, 1898; University Fellow, 1899; 1851 Exhibition Scholar, 1900. For two years worked at research in the Owens College; for one year with Professor Van't Hoff. Joint author of paper "On the Combination of Sulphur Dioxide with Oxygen" (*Journ. Chem. Soc.*, 1900).

Harold B. Dixon. W. T. Lawrence.
W. H. Perkin, jun. Wm. A. Bone.
D. L. Chapman.

Stephenson, Robert, jun.,
Burwell, Cambridgeshire.

Portland Cement Manufacturer. Studied Chemistry for 3 years at Cambridge, and took a degree in the Chemistry special there, period 1894—1897. Have been since then engaged in analytical work in connection with the cement industry.

W. J. Sell. A. Hutchinson.
C. T. Heycock. T. B. Wood.
H. J. H. Fenton.

Templeman, William Henry,
67, Park Street, Spring Bank, Hull.

I am a Student of Chemistry at Hymer's College, Hull, and the

Hull Technical School, and wish to become a Fellow of this Society, so that I shall be able to read its Journal and have access to its Library. I qualified for the University Exhibition in First Class Honours, Chemistry, Intermediate Science Exam., London, 1901.

Thomas Luxton. Thos. A. Nightscales.
Samuel Smiles. *Fred. E. Johnson.*
H. Irving Foster.

Varley, Harold Foy Fleetwood,
22, Strathblaine Road, New Wandsworth, S.W.

Consulting Chemist. Student in Pharmaceutical Society's School under Prof. Dunstan (1895—1896), and in the Analytical Laboratory of Messrs. Helbing and Passmore. Now in the service of the Marconi Telegraph Co.

Wyndham R. Dunstan. H. Helbing.
Edgar E. Horwill. William A. Bone.
John Wilson.

Wade, Frank,
36, Craven Park, Harlesden, N.W.

Analytical Chemist. Assistant Chemist, Chemical Dept., Woolwich Arsenal. A.R.C.S. (Chemistry).

W. Kellner. Chapman Jones.
William A. Tilden. James C. Philip.
W. Palmer Wynne. M. O. Forster.

Wager, Morton,
5, Wilton Street, Batley.

Science Master, Batley Grammar School. Lecturer on Chemistry, Ripon Training College. Student of the Royal College of Science, 1896—1897. Inter. B.Sc. London.

J. R. Denison. Wm. Cranfield.
A. V. C. Fenby. I. Patchett.
A. Peacock.

Wallace, Herbert George,
Axim, West Africa; or Pall Mall Club, London.

Mining Engineer. Student at King's College Metallurgical Laboratory 1896—1897. Studied the Chemistry of the Cyanide Treatment of Gold Ores at the McArthur-Forrest Works, Glasgow. Have been employed to report for mining companies on cyanide process, and am at present Managing Engineer of the Kai Syndicate, Ltd.

A. K. Huntington. W. J. Cousins.
George T. Holloway. *Philip Schidrowitz.*
John S. MacArthur.

Whitehouse, Philip Lewington,
32, Lawrence St. Dowanhill, Glasgow.

Technical Chemist. Student under Professor Mills, F.R.S., D.Sc., LL.D., in Glasgow Technical College for three years. First Prize Technical Chemistry, &c. Five years and a half with Messrs. J. Storer and Co., Ltd., Paint Manufacturers, Glasgow; now as Technical Manager, in which capacity I have been engaged in many chemical investigations, one, conjointly with Dr. Mills, on utilisation of slag as pigment.

Edmund J. Mills. James Robson.
A. Humboldt Sexton. *F. H. Jennison.*
G. G. Henderson.

The following Certificates were authorised by the Council under Bye Law I (3):

Gajjar, Prof. T. K., M.A., B.Sc., M.S.C.I.,
Gingaum, Bombay.

Director, Techno-Chemical Laboratory, Bombay. Organiser and First Principal of the Kala-Bhavan (Polytechnic Institute) of Baroda. Translator of Lehne's Artificial Organic Colouring Matters and Author and Editor of different Gujrati Works and a periodical on Chemistry and Dyeing. Professor of Chemistry, Wilson College, Bombay, and Director of the Techno-Chemical Laboratory, Bombay.

H. N. Bilimoria. William Ramsay.

Jameson, J. S.,
Durban, Natal.

Senior Assistant, Government Laboratory, Natal. Three years Edinburgh University. Four years Government Laboratory.

E. Nevill.

Leahy, Albert William Denis,
Darjeeling, India.

A Major in the Indian Medical Service. Civil Surgeon and Medical Officer of Health, Darjeeling. Superintendent of the Eden Sanitarium. M.D. Univ. Dunelm, 1893. F.R.C.S. Eng., 1881. Formerly Medallist in Practical Chemistry at the Charing Cross School of Medicine. Herbert Scholar and Montifiore Prizeman Army Medical School, Netley.

Alex. Pedler.

Pay, Walter Herbert,
Durban, Natal.

Assistant Chemist, Government Laboratory. For four and a half years Assistant in the Government Laboratory, Natal, and being desirous of availing myself of the Society's publications to further my knowledge of Chemistry.

E. Nevill. **W. S. Stanger Higgs.**

RICHARD CLAY AND SONS LIMITED, LONDON AND BUNGAY.

Issued 10/12/01

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 243.

EXTRAORDINARY GENERAL MEETING.

Erratum in Proceedings, No. 242, p. 208, line 11 (and line 9 of the Circular Letter which accompanied it), for "the words 'the Council,'" read "the last words 'the Council,'" in accordance with text of Requisition printed on pp. 208—209.

December 5th, 1901. Mr. C. E. Groves, F.R.S., Vice-President, in the Chair.

Messrs. George Harker and T. G. Donnan were formally admitted Fellows of the Society.

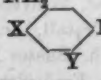
Certificates were read for the first time in favour of Messrs. Harry Burrows, The Green, Southgate, N.; Kenneth Macomb Chance, Lawnside, Edgbaston; William Clifford, 1, Avondale Road, Wolverhampton; John Kemp Smith Dixon, Gothic House, Birstall, nr. Leeds; Alfred Vincent Elsden, Storrington, Pulborough, Sussex; Lewis Eynon, 57, Darenth Road, Stamford Hill, N.; Frederick Ferrand, 13, Torrington Street, Hopwood, Heywood; John Oliver Ferrier, Colombo, Ceylon; George Frederick Holdcroft, 253, Oxford

Street, Manchester; Frank Sturdy Sinnatt, Glenside, Church Lane, Moston, Manchester; Lyon Viccars Turner, Crescent Lodge, St. John's, S.E.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. Frederick T. Allen, B.Sc.; Arthur Baker; Thomas Thorne Baker; Walter Craven Ball, B.A.; Andrew Russell Bennett; Harding Bickford; Henry Boyers; William Burton, B.Sc.; William Cormack; Samuel Irwin Crookes; Frank Crossley, John Howard Davidson, B.Sc.; Francis Davis; Robert English; Henry Wippell Gadd; T. K. Gajjar, M.A., B.Sc.; Hermann Charles T. Gardner; Edward Gillman; William Peer Groves, B.A.; Herbert Blackmore Hammond; Herbert Harding; Edwin Hobson; Beresford Ingram, B.A.; J. S. Jameson; Charles H. Johnson, M.B., Ch.M.; Walter Henry Jollyman; James David Kettle, B.Sc.; J. Bruce-Kingsmill, M.A., B.Sc.; Alfred Tabois Larter; Albert W. D. Leahy; Peter Macdonald; Charles K. Millard, M.D., D.Sc.; Edward Holl Miller; Christian Müller; Herbert Simpson Newbould; Albert Edward Parkes; Walter Herbert Pay; Charles James Tomlin Pollitt; Rowland Samuel Potter; Charles Leonard Royle; John Henry Ryffel, B.A., B.Sc.; Allan Sandford; George Charlton Scott; Edward Charles Sherwood, M.A.; Norman Smith, B.Sc.; Robert Stephenson, jun., B.A.; William Henry Templeman; Harold Foy F. Varley; Frank Wade; Morton Wager; Herbert George Wallace; Philip Lewington Whitehouse.

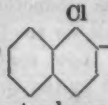
Of the following papers, those marked * were read:

*161. "Influence of substitution on the formation of diazoamines and aminoazo-compounds." By G. T. Morgan, D.Sc.

The disubstituted derivatives of *m*-phenylenediamine having one free para-ortho-position with reference to the amino-radicles interact readily with diazonium salts, giving rise to aminoazo-compounds in almost theoretical quantities. The diamines of the general formula  having substituents in both the para-ortho-positions do not easily condense with diazonium salts, and the yield of aminoazo-compound is very poor.

The bases of both series, however, combine with primulin diazo-

tised on the cotton fibre, the diamines of the first series giving rise to reddish-brown azo-compounds, whilst those of the second series furnish colouring matters having a brownish-yellow tint.

Although the interaction of β-naphthylamine and a diazonium salt leads to the direct formation of an *o*-aminoazo-derivative containing the diazo-residue $R \cdot N_2^-$ in the α-position contiguous to the amino-group, yet 1-chloro-2-naphthylamine, under similar conditions, yields stable diazoamines of the type  In this compound, the azo-group has no tendency to shift into the aromatic nucleus, this transference being apparently prevented by the presence of the chlorine atom in the adjacent ortho-position.

The following acyl derivatives were prepared in characterising certain of the diamines employed in this investigation. *Diformyl*-4 : 6-*diamino*-1 : 3-*xylene*, needles, m. p. 182—183°, the corresponding *diacetyl* and *dibenzoyl* derivatives, m. p. respectively at above 260° and 253°; *diformyl*-2 : 4-*diamino*-1 : 3-*xylene*, m. p. 219—220°, the *diacetyl* derivative, m. p. above 260°, and the *dibenzoyl* derivative, m. p. 232°; *diformyl*-5-*chloro*-2 : 4-*tolylenediamine*, silky needles, m. p. 166°, the *benzoyl* derivative, m. p. 205°.

The following azo-compounds were produced in illustrating the behaviour of the two series of diamines towards diazonium salts. *Benzene*-5-*azo*-2 : 4-*diamino*-1 : 3-*xylene*, readily produced from 2 : 4-diamino-1 : 3-xylene, brown needles, m. p. 208—209°; its *diacetyl* derivative, m. p. above 260°; *diacetylbenzene*-5-*azo*-2 : 4-*tolylenediamine*, m. p. 216—217°.

Benzene-5-*azo*-4 : 6-*diamino*-1 : 3-*xylene*, obtained with some difficulty and in small yield from 4 : 6-diamino-1 : 3-xylene, forms deep red plates, m. p. 182—183°; its *diacetyl* derivative, m. p. above 260°. p-*Toluene*-5-*azo*-4 : 6-*diamino*-1 : 3-*xylene* resembles its lower homologue and melts at 165—166°. Small yields of *benzene*-3-*azo*-5-*chloro*-2 : 4-*tolylenediamine* and its p-*toluene homologue* are produced from 5-chloro-2 : 4-tolylenediamine; they crystallise in dark, brownish-red plates, m. p. 147° and 152° respectively; the *dibenzoyl* derivative of the former azo-compound melts at 236—237°.

Benzene-6-*azo*-2-*chloro*-3 : 5-*tolylenediamine*, obtained in theoretical quantity from 2-chloro-3 : 5-tolylenediamine, forms orange-red, acicular prisms, m. p. 134°; its *diacetyl* and *dibenzoyl* derivatives crystallise in orange-coloured needles, m. p. 251° and 233° respectively.

1-Chloro-2-naphthylamine yields the following diazoamines when treated with the appropriate diazonium chloride. 2-*Diazoamino*-1-*chloronaphthalene*, $ClC_{10}H_6 \cdot N_2H \cdot C_{10}H_6Cl$, produced by the action of

1-chloro-2-naphthalenediazonium chloride, crystallises in golden-yellow needles, m. p. 152°.

p-Nitrobenzene-2-diazoamino-1-chloronaphthalene,

$$NO_2 \cdot C_6H_4 \cdot N_3H \cdot C_{10}H_6Cl,$$

obtained from *p*-nitrobenzenediazonium chloride and 1-chloro-2-naphthylamine, or from 1-chloro-2-naphthalenediazonium chloride and *p*-nitraniline, crystallises in brownish-yellow leaflets; it melts and decomposes at 197—198°. Its production by the two processes indicated shows that Kekulé's rule for the formation of mixed benzenoid diazoamines applies also to those containing naphthalene residues. The *ethyl* derivative, produced by the direct ethylation of the preceding compound, separates from benzene in hard, yellow, prismatic crystals, m. p. 193—194°.

Discussion.

Mr. Evershed asked whether the primulin compounds described were only obtainable on the fibre, and if so, whether similar compounds could be obtained outside the fibre by using dehydrothioparatoluidine instead of primulin.

Dr. Hewitt inquired whether the author expected to obtain three distinct ethyl derivatives of unsymmetrical diazoamino-compounds, or whether the derivative obtained by alkylation would not be a mixture of the other two ethyl derivatives obtained by coupling diazotised amines with monoethylamines. Such cases had already been observed by Meldola. The earlier idea that in the benzene series *p*-azo-compounds exclusively result when the para-position is free can no longer be held to be absolutely true. Bamberger (*Ber.*, 1900, **33**, 3188) has obtained small quantities of ortho-oxyazobenzene mixed with a large amount of the para-isomeride by the action of a phenyldiazonium salt solution on an alkaline solution of phenol.

Dr. Morgan, in reply, said that the colouring matters produced from diazotised primulin were obtained only on the cotton fibre, this reaction being employed merely as a ready means of ascertaining whether the symmetrically disubstituted diamines react with diazo-compounds. The substances prepared by the action of the simpler diazonium salts (benzenediazonium chloride and its *p*-tolyl homologue) on these bases have the appearance of true azo-compounds; they are readily acetylated and benzoylated without decomposition, and withstand prolonged digestion with boiling hydrochloric acid, either in aqueous or alcoholic solutions, just like the isomeric azo-derivatives obtained from the diamines, in which the diazo-residue enters the ring in a para-ortho-position with respect to the amino-radicles.

***162. "The determination of available plant food in soils by the use of dilute solvents." By A. D. Hall and F. J. Plymen.**

The use of various weak acid solvents has been suggested in the analysis of soils, as dissolving out the mineral plant food which may be regarded as immediately "available" for the crop.

In order to ascertain which acid would give the most "critical" results, as judged by the known history of the soil, the authors have determined the phosphoric acid that could be extracted from nineteen different soils by a 1 per cent. solution of citric acid, by equivalent solutions of hydrochloric and acetic acids, by a saturated solution of carbonic acid and by an ammoniacal solution of ammonium citrate respectively. Seven of the soils were from plots on the Broadbalk field, Rothamsted, which had been continuously manured in the same manner for 42 years previously; the remaining twelve were soils of very various origin, which had been the subject of crop experiments and of which the reaction to phosphatic manuring was well marked. In the same seven soils from the Broadbalk field the authors determined the potash extracted by the same solvents, with the exception of ammonium citrate; five other soils of different origin, whose response or otherwise to potash manuring had been tested by experiment, were also examined. Determinations were made of the phosphoric acid and potash dissolved after long digestion with strong hydrochloric acid, of the loss on ignition and of the earthy carbonates present in each soil.

The acids did not attack the phosphates and potash in the same way; in the case of phosphoric acid most was dissolved by citric acid, in the case of potash by hydrochloric acid; water charged with carbonic acid generally dissolved less than the other solvents. In all cases the weak acids gave better indications of the need of the soil for special mineral manuring than was afforded by the determination of the total phosphoric acid or potash present.

Though, as a rule, all the acids gave similar indications as to the relative fertility of the soils, as regards the mineral matters under consideration, certain differences exist in their modes of attack; for example, from the soil of the Broadbalk field, which had received an annual dressing of dung for 42 years, the weak hydrochloric acid extracted a comparatively smaller proportion of phosphoric acid than the other solvents; hydrochloric acid again had relatively slight action on the phosphates of the nitrated plots. The strength of the acids used affected the amount of phosphoric acid dissolved, and the addition of calcium carbonate to the soil diminished the amount dissolved by citric, but not by acetic or carbonic acids.

Though the differences in the rate of attack which the various acids

exhibit in dealing with soils of a different type are related to the varying states of combination of phosphoric acid or potash in the soils, there is still sufficient likeness in the indications afforded by all the acids to negative the idea that any one acid can be found which will discriminate sharply between the "available" and "non-available" mineral plant food.

The authors conclude:

(1) That no sharp distinction can be drawn between "available" and "non-available" phosphoric acid and potash in the soil, and that any process for determining the "available" constituents is an empirical one, dependent on the strength and nature of the acid used.

(2) That the weak solvents give information as to the requirements of a given soil for mineral manures of a far more trustworthy nature than that which is afforded by such a solvent as strong hydrochloric acid.

(3) That of the acids examined, the 1 per cent. solution of citric acid gives results most in agreement with the recorded history of the soil, though there is evidence that the same interpretation cannot be put on results obtained from all types of soil.

Discussion.

Dr. Armstrong said the only way in which the method advocated could be tested was to compare the laboratory results with those afforded by field experiments such as had been made at Rothamsted; and it was remarkable how general was the agreement in that case. But he felt less happy after listening to the account given of this work with other soils: the results did not appear to be so uniformly in favour of Dr. Dyer's method. The conditions offered by soils were obviously very complicated, and it was difficult to believe that so simple a test could afford really comparable results in all cases, especially when applied to soils varying greatly in character. But the case was one in which the decision must be based on considerable experience. Dr. Armstrong took exception to the authors' use of curves in expressing their results, and suggested that only vertical ordinates should be plotted.

Mr. T. S. Dymond said that this paper was particularly interesting, as one of the soils was a London clay from the "derelict" grass land of Essex, from a field which manurial trials had shown to be almost devoid of available phosphoric acid. When superphosphate of lime was used, a dressing of nitrate of soda had doubled the produce of hay, while in its absence nitrate of soda failed to give any increase at all. The citric acid-soluble phosphoric acid in the top nine inches of soil amounted, as shown by the authors, to 200 lbs. per acre, while the crop was able to

remove no more than 2 lbs., leaving, apparently, no further available phosphoric acid in the soil. Although that quantity might be potentially "available" in the soil, it was not actually available in such land as this, until, by improving its mechanical condition, air was admitted, fermentation encouraged, and carbonic acid produced. The experiment also indicated that the acidity of the root sap of the grasses and clovers had little, if any, effect in dissolving "available" phosphate. Both on this ground and on the ground that the carbonic acid-soluble phosphoric acid, as shown by the authors, was much lower than the citric acid-soluble phosphoric acid, the use of carbonic acid as a solvent would appear to give a truer idea of the amount of phosphoric acid actually available. No conclusion as to the manurial requirements of such land should be drawn without also taking into account the various circumstances favourable to carbonic acid production.

Mr. F. J. Lloyd said that, as in the case of Dr. Dyer's paper (*Proc.*, 1894, 10, 36), no steps seemed to have been taken to allow for the alkaline reaction of the soil. In the 200 grams used by the authors there might easily be present 4 grams of calcium carbonate, a quantity which would materially affect the 20 grams of citric acid in 2 litres of solution, so that the soil was not really subjected to the action of a 1 per cent. solvent.

Mr. Hall said, in reply, that the effect produced by calcium carbonate in the soil had not been overlooked. The authors had used a soil to which successive additions of 2, 5, and 10 per cent. of calcium carbonate were made before treating with the dilute acid. The amount of phosphoric acid dissolved by the citric acid was diminished with each addition of calcium carbonate, but the attack of acetic and carbonic acids was practically unchanged. The diminution was not, however, proportional to the neutralisation of the acid, because neutral saline solutions themselves had a solvent effect, dissociation doubtless coming into play.

There were discrepancies still to be cleared up in the results furnished by citric acid; probably as was indicated in the paper, for different types of soil different 'limits' would have to be taken as indicative of the need of mineral manures.

***163. "On a method for determining small quantities of carbonates." By A. D. Hall, and E. J. Russell.**

The authors have devised an apparatus for determining small quantities of carbonates in material like soil by measuring the carbon dioxide evolved. The material is placed in a small bulb, the volume of which need not be known, in which the pressure is reduced to an approximate

vacuum; the carbonate is decomposed by the admission of dilute sulphuric acid, and the change in pressure thus produced is noted. Connection is then made with a second vacuous bulb of known volume, and the change in pressure again read. From the two changes in pressure the volume of carbon dioxide can be calculated. A knowledge of the volume of the material is not required, and the volume of the carbon dioxide which dissolves in the reacting liquid does not enter into the calculation since the liquid practically forms part of the unknown volume of the first bulb.

Examples are given of the measurements of carbon dioxide evolved from pure carbonates in known quantity ranging from 0·13 c.c. to 11·26 c.c.

164. "Derivatives of gallic acid." By F. B. Power and F. Shedden.

The authors have prepared and described the following derivatives of gallic acid.

Ethyl dinitrodiacetylgallate, $C_6(NO_2)_2(C_2H_3O_2)_2OH\cdot CO_2C_2H_5$, was prepared by the nitration of ethyl triacetylgallate, m. p. 133°. It forms lemon-yellow needles, m. p. 165°.

Ethyl dinitrotriacetylgallate, $C_6(NO_2)_2(C_2H_3O_2)_3\cdot CO_2C_2H_5$, was prepared from the preceding compound by the action of acetic anhydride. It forms colourless needles, m. p. 145—146°, which gradually become yellow. Its cold alcoholic solution gives no reaction with ferric chloride, but, on boiling, a bluish-green colour is produced.

Ethyl dinitrogallate, $C_6(NO_2)_2(OH)_3\cdot CO_2C_2H_5$.—When an alcoholic solution of ethyl dinitrodiacetylgallate is boiled with sodium ethoxide and allowed to stand, the *sodium salt* of *ethyl dinitrogallate* was deposited as a bright red, crystalline powder. From the aqueous solution of the latter, hydrochloric acid precipitates ethyl dinitrogallate in the form of small, yellow scales which melt at 153—154°. The same compound was obtained by boiling ethyl dinitrodiacetylgallate with 50 per cent. sulphuric acid.

Ethylmonamidogallate hydrochloride,

$$C_6H(NH_2)(OH)_3\cdot CO_2C_2H_5,HCl,H_2O,$$

was obtained, together with the diamido-derivative, by the reduction of ethyl dinitrogallate with tin and hydrochloric acid. It forms white, needle-shaped crystals, which melt at 210° with decomposition. It can be precipitated from its aqueous solution by the addition of strong hydrochloric acid.

Diazoethylgallate, $\begin{matrix} O\text{———————}N \\ | \\ C_6H(OH)_2CO_2C_2H_5\cdot N \end{matrix}$, was obtained by the action of nitrous acid on ethyl monamidogallate. When recrystallised

from dilute acetic acid it forms fine, reddish-brown needles, which melt with sudden decomposition at 182°. When heated with water in a sealed tube at 220° for four hours, the nitrogen is completely eliminated and ethyl gallate is produced.

Ethyl diamidogallate hydrochloride, $C_6(NH_2)_2(OH)_3 \cdot CO_2C_2H_5,2HCl$, was obtained, together with the above described monamido-derivative, by the reduction of ethyl dinitrogallate. It melts with decomposition at 197°, and is very easily oxidised. It dissolves readily in water, and the solution almost immediately becomes blue, the colour being intensified by the addition of a very little ferric chloride, but destroyed by an excess.

165. "Note on phosphorus suboxide." By K. C. Browning, M.A.

The author has investigated the following methods used to prepare so-called phosphorus "suboxide."

(i) Oxidation of phosphorus, both in the solid state and in solution, by air diluted with carbon dioxide.

(ii) Action of metals on phosphorus oxychloride.

(iii) Action of acetic anhydride on sodium hypophosphite.

The results obtained confirm, on the whole, those of Chapman and Lidbury and of Burgess and Chapman, although the author believes that the suboxide *can* exist under certain conditions.

166. "The bromination of trimethylsuccinic acid and the interaction of ethyl bromotrimethylsuccinate and ethyl sodiocyanacetate." By W. A. Bone and C. H. G. Sprankling.

When trimethylsuccinic acid is heated under pressure to 130° with the calculated quantity of bromine, it is converted into the characteristic white *bromotrimethylsuccinic anhydride*, m. p. 197—198°. On the other hand, if the bromination be carried out according to the Hell-Volhard-Zelinsky (phosphorus and bromine) method and the product be poured into alcohol, a mixture of the bromoanhydride and *ethyl bromotrimethylsuccinate* results, from which it is difficult to obtain the latter substance in a tolerably pure state.

On heating the bromoanhydride with diethylaniline, hydrogen bromide is eliminated, and on afterwards pouring the liquid into a solution of potassium hydroxide, the potassium salt of *methylenedimethylsuccinic acid*, $(CH_3)_2C(CO_2H) \cdot C(CO_2H) : CH_2$, is obtained. The acid melts at 140—141°, its diethyl salt boils at 173—176° (755—760 mm.) and readily absorbs bromine and hydrogen bromide in the cold.

Ethyl bromotrimethylsuccinate reacts with ethyl sodiocyanacetate

with the formation of the cyano-ester which on hydrolysis yields a tribasic acid, $C_9H_{14}O_6$, melting at 137—138°. This acid is not *i*-camphoronic (*aaβ*-trimethyltricarballylic) acid (m. p. 169—173°), which would have resulted had the reaction proceeded normally, thus:

$$(CH_3)_2C(CO_2Et)\cdot C(CH_3)Br(CO_2Et) + NaCH(CN)(CO_2Et) = (CH_3)_2C(CO_2Et)\cdot C(CH_3)(CO_2Et)\cdot CH(CN)(CO_2Et) + NaBr.$$

Most probably the acid is the isomeric *aa-dimethylbutane aa'β-tricarboxylic acid*, a view which the authors' experiments so far justify, and its formation is explained on the supposition that ethyl bromotrimethylsuccinate, in contact with ethyl sodiocyanacetate, loses hydrogen bromide, forming ethyl methylenedimethylsuccinate, which immediately condenses with ethyl cyanacetate as indicated by the equation:

$$(1)\ (CH_3)_2C(CO_2Et)\cdot C(CH_3)Br(CO_2Et) = HBr + (CH_3)_2C(CO_2Et)\cdot C(CO_2Et){:}CH_2.$$

$$(2)\ (CH_3)_2C(CO_2Et)\cdot C(CO_2Et){:}CH_2 + CH_2(CN)(CO_2Et) = (CH_3)_2C(CO_2Et)\cdot CH(CO_2Et)\cdot CH_2\cdot CH(CN)(CO_2Et).$$

The further investigation of the new acid is now being prosecuted.

167. "β-Bromocamphor." By H. E. Armstrong and T. M. Lowry.

The formation of derivatives of β-bromocamphor on decomposing by heat the sulphobromides of the Reychler series of substituted camphorsulphonic acids has been described in a previous notice (this vol., p. 217). On treating the unsubstituted sulphobromide in a similar manner, in the spring of the present year, a bromocamphor was obtained, which melted at 76°, very similar to ordinary bromocamphor; but as the melting point of a mixture of the two substances was 65°, it was clear that they were not identical. By further purification of the substance, the melting point was raised to 79°. The optical rotatory power of the new compound is very different from that of α-bromocamphor, a solution in acetone containing 3·3 per cent. giving $[\alpha]_D = 18°$, the corresponding value for the α-bromocamphor being 143°.

Recently, larger quantities of material have been prepared, and proof has been obtained that the new bromocamphor is the parent term of the β-series by its direct oxidation into β-bromocamphoric acid.

Simultaneously with the authors, Dr. M. O. Forster has obtained β-bromocamphor by simply brominating the isomeride of camphor which he has described under the name of hydroxycamphene. A

direct comparison of the products from the two sources has been made, which leaves no doubt as to their identity. Dr. Forster's observations are described independently.

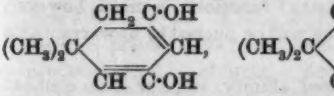
168. "β-Bromocamphor." By M. O. Forster.

When 1-hydroxycamphene (*Trans.*, 1901, 79, 644), dissolved in glacial acetic acid containing sodium acetate (1½ mols.), is treated with a solution of bromine (1 mol.) in the same solvent, water precipitates a new bromocamphor, which, from the fact that bromine converts it readily into β-dibromocamphor melting at 114°, must be regarded as the monobromocamphor which has the substituent in the unknown β-position. The bearing which this observation has upon the constitution of 1-hydroxycamphene will be discussed in a future communication.

β-Bromocamphor, $C_{10}H_{15}OBr$, crystallises from alcohol in long, colourless, prismatic needles and separates from petroleum in transparent, well-formed prisms; it melts at 78°, has $[\alpha]_D = +19°$ in alcohol and $[\alpha]_D = +16°$ in chloroform. Alcoholic potash eliminates bromine from the substance and converts it into an unsaturated acid which belongs probably to the campholenic series. The *oxime* crystallises from alcohol in lustrous, rhomboidal plates, which melt at 156°.

169. "Substituted Dihydrobenzenes. Part I." By A. W. Crossley and H. R. Le Sueur.

When 2:6-diketo-4:4-dimethylhexamethylene (dimethyldihydroresorcinol) is treated with phosphorus pentachloride, both oxygen atoms are removed apparently as hydroxyl groups, giving rise to 2:6-*dichloro*-4:4-*dimethyldihydrobenzene*, a colourless, highly refractive liquid,



It has a faint odour of turpentine, resinifies slowly on exposure to air, and on boiling with dilute sulphuric acid is reconverted into dimethyldihydroresorcinol. When treated with sodium in moist ethereal solution, both chlorine atoms are replaced by hydrogen atoms and there results 4:4-*dimethyldihydrobenzene*, a clear, colourless, mobile liquid, with a marked odour of turpentine, boiling at 111°. It is homologous with the terpenes, which it resembles in chemical behaviour. Thus it decolorises a solution of bromine in chloroform; concentrated sulphuric acid produces a blood red colour, changing to

violet on standing, and with hydrogen bromide it gives a crystalline *hydrobromide*.

Its properties are being thoroughly investigated, and other similar hydrocarbons are being prepared.

170. "The part played by residual affinity in the formation of substitution derivatives. The orienting influence of sulphur." By H. E. Armstrong and E. Horton.

In previous notices, it has been argued that the formation of ortho- and para-substitution derivatives from phenolic and aminic compounds is due to the attractive influence exercised by the oxygen and nitrogen respectively, and experimental evidence has been adduced which shows that if the phenolic or aminic hydrogen be displaced by hydrocarbon or acid radicles, the "activity" of the oxygen or nitrogen is more or less diminished, if not entirely destroyed; in other words, that the "residual affinity" of the negative element becomes weakened in some cases to the point of being inoperative (compare *Proc.*, 1899, **15**, 176; 1900, **16**, 157; *B.A. Report*, 1899, 683).

Although applied to the explanation of the formation of substitution derivatives generally as far back as 1887 (*Trans.*, **51**, 268), the doctrine of "residual affinity" has not hitherto received the attention it perhaps deserves in this connection; we seem to have forgotten that the conception that addition precedes substitution dates back at least to Kekulé's famous paper on the valency of carbon (1858). But now that the doctrine of residual affinity has been rediscovered in Germany by Thiele, and advocated by von Baeyer (*Ber.*, 1901, **34**, 2686), it appears likely to become the fashion, and there is some chance that at last justice may be done to the peculiar qualities of the negative elements; the tendency at the moment to credit oxygen with full tetrad functions is proof, however, that unless care be taken the doctrine will be pushed to unwarrantable extremes.

In studying the influence of residual affinity, sulphur is an element of peculiar interest deserving of far more attention than it has hitherto received; its lethargic behaviour in benzenoid compounds is especially remarkable. To obtain further knowledge of these compounds, the authors are engaged in contrasting the thiobenzenoid ethers with the corresponding oxygen ethers.

Methyl and ethyl phenylsulphides are readily sulphonated, yielding para-acids, which afford well-defined salts, &c. On oxidation by permanganate, the thiosulphonates are converted into corresponding sulphone-sulphonates. If an aqueous solution of the thiosulphonate be sub-

jected to the action of bromine, it is converted wholly into the corresponding sulphoxide-sulphonate; for example, $EtS\cdot C_6H_4\cdot SO_3K + Br_2 + OH_2 = EtSO\cdot C_6H_4\cdot SO_3K + 2HBr$, the bromine acting only as an oxidising agent. As it was probable that oxidation was due to the formation of hypobromous acid, in the expectation that if this were prevented from forming, bromine would be without action, the salt was brominated in presence of muriatic acid; under these conditions, the salt was converted entirely into the ortho-bromothio-sulphonate. It seems, therefore, that, if prevented from undergoing oxidation, sulphur may behave as oxygen does; but the thioether-sulphonates are far more stable than the oxygen-ether-sulphonates, as the sulpho-group is not displaced from them by bromine.

Mr. Lewis has ascertained that muriatic acid has, in some cases, a distinct influence on the course of change on brominating the oxygen-ether-sulphonates, and that it promotes the formation of the ortho-bromosulphonate whilst diminishing the extent to which the sulphonic group is displaced.

ADDITIONS TO THE LIBRARY.

I. By Donation.

Church, A. H. The Chemistry of Paints and Painting. Third edition, revised and enlarged. 8vo, pp. 355. London. 1901.
From the Author,

Goppelsroeder, Friedrich. Capillaranalyse, beruhend auf Capillaritäts- u. Adsorptionserscheinungen, mit dem Schlusskapitel: das Emporsteigen der Farbstoffe in den Pflanzen. Mit 59 Tafeln. 8vo, pp. 545. Basel. 1901. From the Author.

van't Hoff, J. H. Vorlesungen über theoretische und physikalische Chemie. Erstes Heft: die chemische Dynamik. Mit in den Text eingedruckten Abbildungen. Zweite Auflage. 8vo, pp. 251.
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II. By Purchase.

Fischer, Ferdinand. Die Brenstoffe Deutschlands und der übrigen Länder der Erde und die Kohlennoth. Mit einer graphischen Darstellung. 8vo, pp. 107. Braunschweig. 1901.

von Georgievics, Georg. Lehrbuch der Farbenchemie. Zweite Auflage. 8vo, pp. 449. Leipzig und Wien. 1902.

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Stenglein, M. Handbuch der Presshefen-Fabrikation. Erste Abtheilung: die Apparate u. Einrichtung von Presshefefabriken, mit 251 Abbildungen. Zweite Abtheilung: das chemische u. das mikroskopische Laboratorium des Hefebrenners, mit 125 Abbildungen u. 12 Tafeln (*being* Nos. 61 and 62 of Bolley's Technologie, Bd. iv, 5, 1, 2). 8vo, pp. 327, 279. Braunschweig. 1901.

LIBRARY CATALOGUE.

A new Catalogue of the Library, arranged under authors' names and subjects in accordance with the system adopted in indexing the Society's publications, is ready for the press. Fellows who desire a copy of the Catalogue, at a cost of 2*s*. 6*d*., are requested to send in their names to the Secretaries not later than January 31st, 1902.

If a sufficient number of names is not received, the catalogue will not be printed.

MEMORIAL LECTURES, 1893—1900.

Fellows can now obtain copies of the volume of collected Memorial Lectures on application to the Assistant Secretary, price 7*s*. 6*d*. post free.

At the next ordinary meeting, on Thursday, December 19th, the following papers will be communicated:

"Corydaline. Part VII. The constitution of corydaline." By J. J. Dobbie, M.A., D.Sc., and A. Lauder, B.Sc.

"The relation of corydaline to berberine. The oxidation of berberine with nitric acid." By J. J. Dobbie, M.A., D.Sc., and A. Lauder, B.Sc.

"The magnetic rotation of some polyhydric alcohols, hexoses, and disaccharoses." By W. H. Perkin, sen., Ph.D., F.R.S.

"Stereoisomeric halogen derivatives of α-benzoylcamphor." By M. O. Forster and F. M. G. Micklethwait.

"Is argon an elementary substance?" By G. Martin.

RICHARD CLAY AND SONS LIMITED LONDON AND BUNGAY

Issued 31/12/01

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 17. No. 244.

Extraordinary General Meeting, December 12th, 1901. Professor EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

The PRESIDENT stated that this meeting had been convened in accordance with a requisition signed by 128 Fellows of the Society and that the following motions would be proposed:

(1) On line 7 of Bye-Law XI (page 21, fifth line from top) to delete the words "the Council" and insert in their place the words "an Extraordinary General Meeting of the Society."

(2) To resolve that the Ordinary Meetings of the Society shall continue to take place, as heretofore, on Thursdays, at 8 p.m.

Motion (1) was proposed by Mr. HEHNER and seconded by Mr. PAKES.

Professor FRANKLAND proposed, and Professor RAMSAY seconded, the following amendment:

"That this meeting desires to express its continued confidence in the Council as the Executive of the Society, as it has no reason to doubt that all the business of the Society, including the selection of days and hours of meeting, will be managed as heretofore in the interests of the Society as a whole and in accordance with the wishes of the majority of the Fellows."

After a discussion in which the following Fellows took part: Dr. Divers, Mr. A. H. Allen, Mr. D. L. Howard, Professor Smithells, Dr. Lewkowitsch, Professor Dewar, Professor Warington, and Mr. Phipson Beale, K.C., the President asked for a show of hands and declared the amendment carried. A poll having been demanded, the President announced that it would be taken by means of cards having "For" and "Against" printed on them, with a space for the

signature of the Fellow voting, one of these words to be deleted. Mr. Heycock, Dr. Hewitt, Dr. Shields, and Dr. Travers, having been appointed scrutators,

The PRESIDENT announced that the votes were, for the amendment, 128; against, 120.

The PRESIDENT then declared the following carried:

"That this Meeting desires to express its continued confidence in the Council as the Executive of the Society, as it has no reason to doubt that all the business of the Society, including the selection of days and hours of meeting, will be managed as heretofore in the interests of the Society as a whole and in accordance with the wishes of the majority of the Fellows.

December 19th, 1901. Prof. J. EMERSON REYNOLDS, F.R.S., President, in the Chair.

Messrs. Kiddell, Larter, Harding, and H. C. T. Gardner were formally admitted Fellows of the Society.

The SECRETARY read the following Address which was presented on November 24th to Professor Berthelot in the name of the Chemical Society by the President, who was accompanied by Dr. Gladstone and Professor Ramsay, as the representatives of the Society.

To M. MARCELLIN BERTHELOT, *Senator, late Minister for Foreign Affairs, Member of the Institute.*

SIR,

On behalf of the President, Officers, Council, and Fellows of the Chemical Society, we beg to offer you, the Senior Foreign Member of our Society, our heartiest congratulations on the occasion of the Fiftieth Anniversary of your first scientific publication.

The Chemical Society has recently received the first volumes of your monumental work, yet to be completed, including the great number of papers which you have contributed, during fifty years of scientific activity, to the Chemistry of the hydrocarbons and their methods of formation.

There is, however, scarcely any department of Chemical Science in which you have not worked as a pioneer with distinguished results, whilst to you is largely due the foundation of a new branch of the Science, namely, Thermo-Chemistry.

Alike in the history of our Science, and in its applications to Agriculture and Industry, you have made brilliant contributions.

We trust that for many years you may possess the health and strength to continue those investigations which have made your name famous throughout the Scientific world.

Signed, on behalf of the Chemical Society,

J. EMERSON REYNOLDS, *President.*
WILLIAM A. TILDEN, *Treasurer,*
WYNDHAM R. DUNSTAN, } *Secretaries.*
ALEXANDER SCOTT, }
RAPHAEL MELDOLA, *Foreign Secretary.*

November 22nd, 1901.

DAY AND HOUR OF MEETING.

The PRESIDENT announced that at the Meeting of Council held this afternoon, the following resolution was unanimously adopted:

"That having regard to the discussion which took place at the Extraordinary General Meeting on December 12th, the Council resolves to make the experiment of holding the Ordinary Meetings, as far as possible, alternately at 5.30 p.m. on Wednesdays, and at 8 p.m. on Thursdays, from January, 1902, until the end of the present session in June, instead of holding meetings on Wednesdays at 5.30 p.m. only during the period from January to March, 1902, as stated in the resolution of July 4th, 1901, which is hereby rescinded,"

and that a Committee had been appointed consisting of the President, the Treasurer, the Senior Secretary, Dr. Armstrong, Professor Dobbie, and Dr. Forster to arrange the exact dates on which future meetings during the session should be held.

The next Ordinary Meeting of the Society will be held on Thursday, January 16th, at 8 p.m.

It was also announced that Sir Henry Roscoe had presented a plaster cast of the bronze portrait on Bunsen's tomb in Heidelberg, and that a photograph of a bas-relief of Professor Julius Thomsen had been presented to the Society by Mr. Harald Faber.

Certificates were read for the first time in favour of Messrs. Evelyn Andros de la Rue, 52, Cadogan Sq., S.W.; Keith Benham Benham, Deans Hall, Stafford; William Dennis, Ocean Road Pharmacy, South Shields; Paul Haas, 11, Westbourne Park Rd., W.; Eugene Edwin Hennessey, Bigods, Dunmow, Essex; William Holdsworth Hurtley, St. Bartholomew's Hospital, E.C.; David Smith Jardin, Rathgar House, Rathgar; Harry Lucas, 1, St. Agnes' Place, Kennington Park, S.E.; John Ross MacKenzie, 31, Bailey St., Ton-Pentre, Glam.; William Maitland, 236, Brookhill, Sheffield; Francis Martin, 64,

Samuel St., Woolwich; Francis Hylton Molesworth, Turramurra, Sydney, N.S.W.; Alfred Holley Mundey, 17, St. Margaret's Rd., Plumstead; Robert Eley Blake Smith, 93, Upper Richmond Rd., Putney, S.W.; William Southworth, County Council Farm, Hutton, Preston, Lancs.

Of the following papers those marked * were read:

*171. "Corydaline. Part VII. The constitution of corydaline." By J. J. Dobbie, D.Sc., M.A., and A. Lauder, B.Sc.

The decomposition products of corydaline have been studied by the authors in greater detail with the following results. The acid, $C_6H_4N(CO_2H)_3$, obtained by oxidising corydaline (*Trans.*, 1897, 71, 657), is, by long-continued heating with potassium permanganate in alkaline solution, converted into 2 : 3 : 4 : 6-pyridinetetracarboxylic acid. The acid, $C_6H_4N(CO_2H)_3$, must therefore either be 2—CH_3 3 : 4 : 6-pyridinetricarboxylic acid or 2—CH_3 4 : 5 : 6-pyridinetricarboxylic acid. From what follows, the former formula is probably the correct one.

Corydilic acid, $C_{12}H_6N(OCH_3)_2(CO_2H)_3$ (*Trans.*, 1897, 71, 657), is soluble in hydrochloric acid and under certain conditions forms an unstable hydrochloride. When boiled with potassium permanganate, it is split up into a mixture of meta-hemipinic acid and the acid $C_6H_4N(CO_2H)_3$.

When corydic acid (*Trans.*, 1897, 71, 657), $C_{14}H_9N(OCH_3)_2(CO_2H)_2$, is oxidised with permanganate at the ordinary temperature, it yields a yellow, dibasic acid, $C_{12}H_5N(OCH_3)_2(CO_2H)_2$, which contains the two methoxyl groups of corydic acid.

Mild oxidising agents remove four atoms of hydrogen from corydaline and convert it into dehydrocorydaline, an intensely yellow coloured base (*Trans.*, 1897, 71, 657). Berberine is also a yellow coloured base, but readily takes up four atoms of hydrogen, forming colourless tetrahydroberberine. Corydaline therefore corresponds to tetrahydroberberine and dehydrocorydaline to berberine.

Corydaline (colourless).	Tetrahydroberberine (colourless).
$C_{22}H_{27}NO_4$.	$C_{20}H_{21}NO_4$.
Dehydrocorydaline (yellow).	Berberine (yellow).
$C_{22}H_{23}NO_4$.	$C_{20}H_{17}NO_4$.

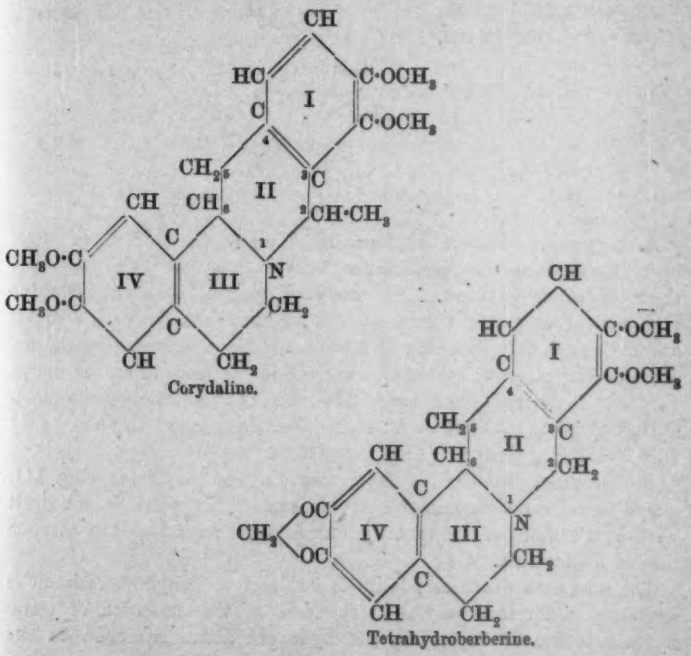
The four oxygen atoms of corydaline are all present in methoxyl groups (*Trans.*, 1892, 61, 605). When oxidised with potassium permanganate at 100°, corydaline yields a mixture of hemipinic and meta-hemipinic acids, together with corydaldine, $C_{11}H_{13}NO_3$, a neutral substance of which the yield is larger when the oxidation takes place

at the ordinary temperature. This substance has been shown to be an *iso*quinoline derivative.

When oxidised with dilute nitric acid, corydaline, $C_{22}H_{27}NO_4$, is first converted into dehydrocorydaline, $C_{22}H_{23}NO_4$; further oxidation splits off one of the benzene rings and yields corydic acid, a yellow, crystalline substance (*Trans.*, 1897, 71, 657). Corydic acid in turn, when oxidised at 100° with permanganate, yields meta-hemipinic acid, the acid $C_6H_4N(CO_2H)_3$, and the highly insoluble, colourless corydilic acid, $C_{12}H_6N(OCH_3)_2(CO_2H)_3$, which, on further oxidation with permanganate, is entirely resolved into meta-hemipinic acid and the acid $C_6H_4N(CO_2H)_3$.

As the acid $C_6H_4N(CO_2H)_3$ contains six atoms of carbon in addition to the carbon atoms of the carboxyl groups, it cannot be derived from the *iso*quinoline nucleus which has no methyl group attached to it, but must represent a fourth ring, and the nitrogen atom must, as in the case of berberine, be common to two rings.

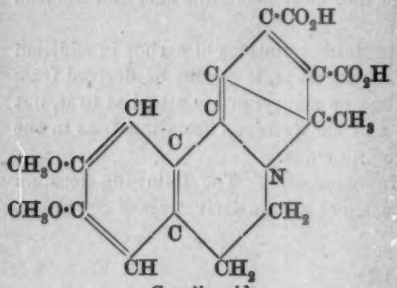
There are thus four rings in corydaline. The following formula satisfactorily explains the formation of all the derivatives of corydaline which have been examined.



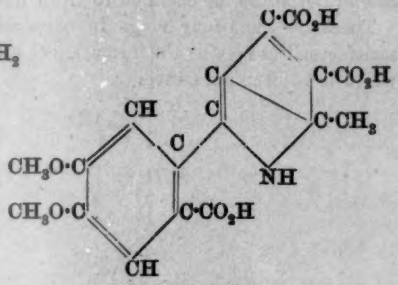
Corydaline.

Tetrahydroberberine.

By oxidation, rings I and IV would yield hemipinic and meta-hemipinic acids respectively; ring II, the acid $C_6H_4N(CO_2H)_3$. Corydaldine, $CH_3O>C_6H_2<CO-NH / CH_3O \quad CH_2\cdot CH_2$, contains rings III and IV, and would result from the oxidation of corydaline, just as ω-amidoethylpiperonylcarboxylic anhydride results from the oxidation of berberine. Corydic acid would be formed by the destruction of ring I, and corydilic acid from corydic acid by the oxidation of ring III. The formulæ of the last-mentioned acids are therefore:



Corydic acid.



Corydilic acid.

A comparison between the formulæ of corydaline and tetrahydroberberine explains the resemblance between the two substances and their oxidation products. By oxidation, ring I, both in berberine and corydaline, yields hemipinic acid; ring IV in berberine yields hydrastic acid, corresponding to meta-hemipinic acid from corydaline. ω-Amidoethylpiperonylcarboxylic anhydride, corresponding to corydaldine, is derived from rings III and IV, and berberonic acid, $C_5H_2N(CO_2H)_3$ $[(CO_2H)_3 = 3:4:6]$, corresponding to the acid $C_6H_4N(CO_2H)_3$, from ring II in corydaline.

Berberonic acid is derived from ring II, and not from ring III, which would yield carbocinchomeronic acid. This point is not dealt with by Perkin, but incidentally affords confirmation of the correctness of his formula.

The ease with which corydaline is oxidised to dehydrocorydaline is explained in the same way as in the case of the oxidation of tetrahydroberberine to berberine, the hydrogen atoms attached to the

carbon atoms 2, 5, and 6 of ring II being removed on oxidation, and a link established between the atoms 2 and 5, and a second link between 5 and 6.

The above formula for corydaline, which accounts for its decomposition products and explains the analogies with berberine, involves the adoption of the constitution $2\text{–}CH_3 : 3 : 4 : 6$ for the acid $C_6H_4N(CO_2H)_3$; the alternative formula would leave the resemblance to berberine unexplained.

***172. "The relation of corydaline to berberine; the oxidation of berberine with nitric acid." By J. J. Dobbie, D.Sc., M.A., and A. Lauder, B.Sc.**

In the previous abstract it is shown that the constitution of corydaline can be expressed by a formula similar to one of the formulæ proposed by Perkin for berberine.

Assuming the correctness of the formula for corydaline, the absence of compounds corresponding to berberal and berberilic acid (Perkin, *Trans.*, 1890, 57, 992) from amongst the decomposition products of corydaline is explained, since all these substances contain an atom of oxygen united to the carbon atom 2 in ring II (see previous abstract), where owing to the presence of the methyl group it is impossible to introduce an oxygen atom into corydaline derivatives. If the view of the relation of the two substances expressed in the formulæ is correct, the first of Perkin's alternative formulæ (Perkin, *Trans.*, 1890, 57, 992) must be adopted. In his second formula, a double bond is shown between the carbon atoms 2 and 5 of ring II. No double bond in this position is possible in dehydrocorydaline on account of the presence of the methyl group, and the analogy between the two substances breaks down if we suppose the double bond in ring II to occupy different positions. Whilst the absence of certain decomposition products is thus satisfactorily accounted for, the formation of corydic acid from corydaline suggests the possible formation of a similar acid from berberine. By oxidising berberine with dilute nitric acid in exactly the same way as was followed in the preparation of corydic acid (*Trans.*, 1897, 71, 657), an acid, $C_{16}H_{11}NO_6$ (m. p. 285°), was obtained closely resembling corydic acid in properties and obviously bearing to berberine the same relation as corydic acid to corydaline. This acid is very difficultly soluble in hot water; it dissolves in sodium hydroxide, forming a blood-red solution. It is dibasic, almost all its salts are soluble, a notable exception being the acid silver salt. It contains no methoxyl groups, hence (as in the case of corydaline) it is formed by the destruction of ring I. By oxidation with potassium

permanganate, it yields berberonic acid, $C_5H_2N(CO_2H)_3$ [$(CO_2H)_3 = 3:4:6$], and ω-amidoethylpiperonylcarboxylic anhydride. The name *berberidic* is proposed for this new acid.

***173. "The magnetic rotation of some polyhydric alcohols, hexoses and disaccharoses." By W. H. Perkin, sen., Ph.D., F.R.S.**

The object of this investigation was to see if any clue could be obtained from the magnetic rotation of the sugars as to the cause of their bi- or multi-rotation. Some of the polyhydric alcohols were also examined in order that data might be obtained from which to calculate the probable values for the various sugars.

From the rotations obtained for glucose and for fructose, it was found that the suggestion that bi-rotation was due to hydration was untenable. The magnetic rotations are too low for substances possessing the aldehydic and ketonic constitutions usually assigned to these sugars, but they correspond with substances containing an oxygen atom linked as in ethylene oxide or the lactones, all of which give low numbers. This agrees with the suggestion of Lowry (*Trans.*, 1899, 75, 215), that when in solution and having undergone the largest amount of change, glucose exists chiefly in an isomeric form for which he gave two formulæ, of which the more probable one, judging from the magnetic rotation, may be represented thus,

$$CH_2OH{\cdot}CH{\cdot}OH{\cdot}\underset{\displaystyle\text{O}}{\overset{\displaystyle\text{———}}{CH{\cdot}CH{\cdot}OH{\cdot}CH{\cdot}OH{\cdot}CHOH}}.$$

This is the formula originally proposed by Tollens for dry glucose (*Ber.*, 1883, 16, 92). When slightly modified it can also be used to represent fructose in an isomeric condition, equally consistent with the magnetic rotation of this substance in solution.

Saccharose may be regarded as built up from glucose and fructose, both being in their isomeric forms, with elimination of water, its constitution being that proposed by E. Fischer (*Ber.*, 1893, 26, 2405), which is a slight modification of that suggested by Tollens (*Ber.*, 1883, 16, 923).

Maltose and lactose, which possess both birotation and reducing power, appear to have analogous structures, the formula proposed by Fischer for lactose (*loc. cit.*) being practically applicable to both, but their constitution is different from that of saccharose. Hence maltose and lactose are formed from a molecule of glucose or of galactose in the isomeric condition, *plus* a molecule of glucose in the ordinary or aldehydic form, *minus* water, the aldehydic part undergoing isomeric change to a greater or less extent when these disaccharoses are dissolved in water; in this way the possession of birotation by these substances may be explained.

***174. "Stereoisomeric halogen derivatives of α-benzoylcamphor." By M. O. Forster and Miss F. M. G. Micklethwait.**

α'-Benzoyl-α-bromocamphor, $C_8H_{14}<\begin{matrix}CBr\cdot CO\cdot C_6H_5\\CO\end{matrix}$, prepared by dissolving 1-hydroxy-2-benzoylcamphene in glacial acetic acid containing sodium acetate (1½ mols.) and adding a solution of bromine (1 mol.) in acetic acid, crystallises from light petroleum in large, transparent, six-sided prisms and melts at 114°; dissolved in benzene it has $[\alpha]_D = -10{\cdot}0°$, and in chloroform $[\alpha]_D = +10{\cdot}3°$.

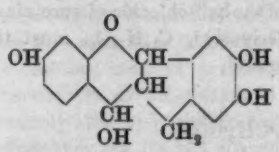
α-Benzoyl-α'-bromocamphor is formed in preponderating amount when potassium hypobromite acts on hydroxybenzoylcamphene dissolved in potash; it crystallises from hot alcohol in transparent, rectangular plates melting at 214°, and has $[\alpha]_D = -53{\cdot}2°$ in benzene and $[\alpha]_D = -19{\cdot}3°$ in chloroform. Hydrogen bromide converts the low melting isomeride into the less readily fusible modification.

α'-Benzoyl-α-chlorocamphor, $C_8H_{14}<\begin{matrix}CCl\cdot CO\cdot C_6H_5\\CO\end{matrix}$, obtained by the action of sodium hypochlorite on hydroxybenzoylcamphene, melts at 88°, and has $[\alpha]_D = -27{\cdot}9°$ in chloroform.

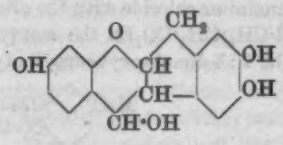
α-Benzoyl-α'-chlorocamphor is produced in the same way and separated by means of its sparing solubility in alcohol; it melts at 219° and has $[\alpha]_D = +26{\cdot}2°$ in chloroform.

***175. "Brasilin and hæmatoxylin. Part VI. The constitution of brasilic acid, of brasilin and of hæmatoxylin." By W. H. Perkin, jun.**

In part I of this research (A. W. Gilbody, W. H. Perkin, jun., and J. Yates, *Trans.*, 1901, 79, 1401), it was argued that since trimethylbrasilin on oxidation with permanganate yields 2-carboxy-5-methoxyphenoxyacetic acid and meta-hemipinic acid, the constitution of brasilin must be represented by one of the following formulæ:



I.



II.

In order to decide between these two formulæ, the author has submitted brasilic acid to a detailed examination and has obtained results which show clearly that formula I must be accepted as representing the constitution of brasilin.

Brasilic acid, $C_{12}H_{12}O_6$, is produced by the oxidation of trimethylbrasilin with permanganate, but the yield is only 0·7 per cent.; it is a monobasic acid, the *silver* salt having the formula $C_{12}H_{11}AgO_6$. The sodium salt, $C_{12}H_{11}NaO_6$, is comparatively sparingly soluble and crystallises in glistening plates.

Since brasilic acid contains one methoxyl group, its formula may be written $MeO{\cdot}C_{10}H_6O_3{\cdot}CO_2H$, and as on fusion with potash it yields a substance which with ferric chloride gives a violet coloration, it is evidently derived from the resorcyl nucleus of brasilin. Furthermore, it yields an oily oxime, $MeO{\cdot}C_9H_3O_2(C{:}NOH)CO_2H$, and when reduced with sodium amalgam it is converted into the *lactone* of *dihydrobrasilic acid*, $C_{12}H_{12}O_5$, which melts at 144° and is very sparingly soluble in ether.

From this behaviour, it follows that brasilic acid contains a carbonyl group, and that this is probably in the γ-position in relation to the carboxyl group.

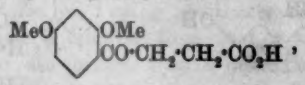
When warmed with sulphuric acid, brasilic acid loses one molecule of water and is converted into *dehydrobrasilic acid*, $C_{12}H_{10}O_5$, a monobasic acid, which is very sparingly soluble in water, melts at 197°, and when treated with permanganate in the cold is oxidised with formation of *p*-methoxysalicylic acid, $MeO{\cdot}C_6H_3(OH){\cdot}CO_2H$.

Hydroxylamine converts dehydrobrasilic acid into an oxime, $C_{12}H_{11}NO_5$, which melts at 172°. The acid, therefore, still contains a carbonyl group. When digested with baryta water, it is readily decomposed with formation of formic acid and a new acid, $C_{11}H_{12}O_5$.

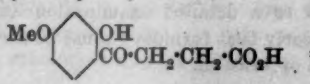
$$C_{12}H_{10}O_5 + 2H_2O = H{\cdot}CO_2H + C_{11}H_{12}O_5.$$

This new acid crystallises from water in colourless needles, melts at 155° and gives, in aqueous solution, an intense violet coloration with ferric chloride; when heated with sodium methoxide and methyl iodide it yields a methyl derivative, $C_{12}H_{14}O_5$, which melts at 147°.

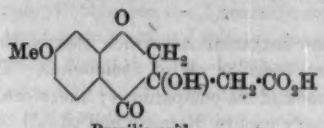
In conjunction with Mr. E. Ormerod, the author has succeeded in synthesising this latter by treating dimethylresorcinol in the presence of aluminium chloride with the ester of the half-chloride of succinic acid, $COCl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, the methyl derivative, $C_{12}H_{14}O_5$, must therefore be 2 : 4-dimethoxybenzoylbutyric acid,



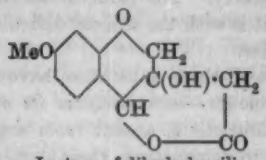
and the acid, $C_{11}H_{12}O_5$, from which it is derived by methylation, is 2-hydroxy-4-methoxybenzoylbutyric acid,



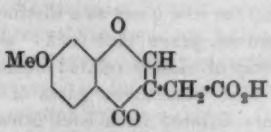
The constitutions of the other acids mentioned above are now established, and are as follows:



Brasilic acid.



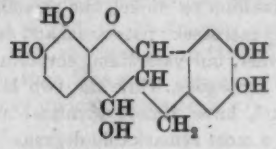
Lactone of dihydrobrasilic acid.



Dehydrobrasilic acid.

Since, of the two formulæ for brasilin given above, formula I alone accounts, in a simple manner, for the formation of brasilic acid, it appears to the author that this must be accepted as representing the constitution of brasilin.

It has already been shown (*Proc.*, 1900, 16, 107) that tetramethylhæmatoxylin, on oxidation with permanganate, gives products which are exactly similar to those obtained from trimethylbrasilin, and there can, therefore, scarcely be a doubt that the constitutional formula of hæmatoxylin is



176. "Is argon an elementary substance?" By G. Martin.

Some eighty distinct elementary substances are now recognised. These are assumed to be composed of different kinds of matter because each one has *chemical properties* peculiar to itself alone. Physical properties are of little value in deciding whether different substances are merely allotropic modifications of one kind of elementary matter, or whether they are distinct elements. The only certain test lies in the *chemical nature* of the compounds produced when the elements unite with other elements.

Elements often resemble each other so strongly in their physical nature that it is almost impossible to distinguish between them. For example, the new radio-active elements are so similar to bismuth,

barium and titanium, that many chemists still hesitate to believe them elementary. The rare earths are composed of elements so much alike that it is with the utmost difficulty they can be distinguished from one another.

But all these substances have one characteristic which stamps them as elements—*each produces its own peculiar set of compounds.* This characteristic is absent from argon and its companions; therefore, in order to demonstrate their elementary nature, Ramsay had to fall back on their physical properties—the most untrustworthy of all methods.

These properties stamp the new gases as a distinct class of elements; but they do not, and cannot, prove that each "element" is a single substance and not a *group* of closely related elements. For instance, were *argon* a *mixture* of 3 monatomic gases of like nature, and of which the atomic weights differed from each other by a fraction of a unit—as do those of nickel and cobalt—it would be impossible to distinguish the mixture from an element. It would answer to exactly the same physical tests and could not be resolved into its compounds by any *physical methods* except with the utmost difficulty. It takes many thousands of fractionations to distinguish between two rare earths, which not only give different chemical compounds, but are far more unlike chemically than would be 3 *monatomic inert gases.*

We are peculiarly liable in the eighth group to meet with neighbouring elements of almost identical atomic weight and properties. For instance, in series 4 of the periodic table, as we advance with increasing atomic weight from potassium to nickel, the resemblance between successive elements steadily increases; potassium and calcium, for example, are quite unlike each other, but vanadium, chromium, manganese, and iron are all strikingly analogous, while the two last elements of the series, cobalt and nickel, have almost identical atomic weights and resemble each other in a most remarkable degree.

In many of the other series, also, we end up in the eighth group with elements so very similar that they are classed as "triads," for example, ruthenium, rhodium, and palladium; osmium, iridium, and platinum; the atomic weights of these triads are in every case very close together.

If each of the "elements" of Ramsay really consists of three allied substances, the eighth group of the periodic table would lose altogether its peculiar "triad" character and split up into three distinct groups—a possibility which of late years has been running through many minds.

177. "The action of phosphorus trithiocyanate on alcohol." By Augustus Edward Dixon, M.D.

Lössner states in a brief preliminary note (*J. prakt. Chem.*, 1873, ii, 7, 474) that phosphorus trichloride, acting upon an alcoholic solution of

potassium thiocyanate, produces a substance crystallising in fin needles, and having the formula $C_5H_{18}N_4S_4O$.

From results obtained by the author in his study of phosphorous and phosphoryl 'thiocyanates,' recently commenced (*Trans.*, 1901, 79, 541), it seemed probable that Lössner's compound, if really formed, must have originated through some decomposition of the phosphorus trithiotriurethane, $P(NH{\cdot}CS{\cdot}OEt)_3$, which might be expected to result from the union of phosphorus trithiocyanate, $P(SCN)_3$, or $P(NCS)_3$, with the alcohol used as solvent; to ascertain if this was the case, the two latter substances were caused to interact directly, in presence of dry benzene.

Phosphorus trithiotriurethane could not be identified; neither could Lössner's compound: thiocyanic acid was expelled, and the residual liquid was eventually resolved into (1) an acid oil, containing phosphorus, and (2) *iso*persulphocyanic acid.

Phosphorus trichloride interacted violently with alcoholic potassium thiocyanate: potassium chloride was precipitated, thiocyanic acid is given off, and from the residual oily liquid, after concentration, *iso*persulphocyanic acid was deposited: no sign could be got of the presence of the compound $C_5H_{16}N_4S_4O$.

The author supposes the *iso*persulphocyanic acid, which is formed in small relative amount in either process, to be produced through the interaction of the mineral acid with the thiocyanic acid simultaneously liberated.

Benzyl alcohol interacts spontaneously with phosphorus trithiocyanate, but, as in the case of ethyl alcohol, no evidence could be obtained of the existence of a salt of phosphorus trithiotricarbamic acid, $P(NH{\cdot}CS{\cdot}OH)_3$; if such compounds are formed at all in these interactions, it is probable that, like their congeners of the thiocarbamidic class, they very readily undergo hydrolysis.

178. "The influence of salts and other substances on the vapour pressure of aqueous ammonia solution." By E. P. Perman.

The author has investigated the effect produced by urea, mannite, potassium sulphate, ammonium chloride, and copper sulphate respectively on the vapour pressure of aqueous ammonia solution by a method similar to that described for sodium sulphate (*Trans.*, 1901, 79, 725). The objects of the research were to find (1) the effect upon the pressure of substances which have no direct chemical action on the ammonia, (2) the effect of rise of temperature on copper sulphate ammonia solution, (3) evidence for or against the existence of hydrates in solution.

The conclusions arrived at by the author are: (1) that salts of the alkalis have a great effect in raising the pressure, but that the effect of

other substances which might be expected to have no direct chemical action on the ammonia is either small or nothing.

(2) That copper sulphate forms complexes with ammonia in solution which tend to decompose on heating, especially when the proportion of copper sulphate is small.

(3) The effect of potassium sulphate is similar to that of sodium sulphate in raising the pressure. There is but little reason to suspect the existence of a hydrate of potassium sulphate, as it crystallises without water; consequently it would appear that neither sulphate exists in solution as a hydrate.

179. "The action of sodium hypochlorite on benzenesulphonanilide. Preliminary notice." By J. B. Cohen and J. T. Thompson.

In the preparation of the different isomeric dichlorotoluenes (Cohen and Dakin, *Trans.*, 1901, 79, 1111), the authors had frequent recourse to the method of chlorination recently studied by Chattaway and Orton (*Trans.*, 1899, 75, 1046; 1900, 77, 134 and 789, and *Ber.*, 1899, 32, 3573). The authors have found that a very similar reaction occurs with the aromatic sulphonanilides, of which, with Dr. Chattaway's friendly acquiescence, the authors now give a brief notice. Twenty grams of benzenesulphonanilide were dissolved in 200 c.c. of a solution of sodium hypochlorite (1 c.c. = 0·03 gram Cl) in the cold and allowed to stand 12 hours. The brown solution was acidified with acetic acid until the buff precipitate redissolved, when it was extracted with chloroform. After rapidly evaporating off the solvent, the residual red liquid was digested for an hour with two volumes of glacial acetic acid containing a few drops of concentrated sulphuric acid, until, on pouring into water, a solid substance separated. The new compound was recrystallised from acetic acid and then from alcohol, when it melted at 129—130°. The yield amounted to 18 grams of crude or 11 grams of purified substance.

The mother liquor contained a small quantity of a semi-solid substance, which became crystalline on standing and after recrystallisation from benzene and petroleum melted at 116°. This substance is probably the benzenesulphonyl-*p*-chloranilide (m. p. 121°), but it is difficult to free it from oily impurity. The substance melting at 129—130° was analysed, with the following result:

0·292 gave 14·15 c.c. moist nitrogen at 15·5° and 758 mm. N = 5·66.
0·3185 „ 0·1764 AgCl. Cl = 13·57.
0·2097 „ 0·1820 $BaSO_4$. S = 11·93.

$C_{12}H_{10}O_2NSCl$ requires N = 5·23; Cl = 13·27; S = 11·90.

In order to determine the constitution of the substance, it was hydrolysed. Two grams were heated with about eight grams of concentrated hydrochloric acid in a sealed tube to 190° for 4—5 hours. On opening the tube, there was a strong smell of benzene, the presence of which was confirmed by extracting with light petroleum, nitrating the extract with a mixture of concentrated sulphuric and nitric acids, washing, and evaporating off the light petroleum. On reducing the residue with zinc dust and acetic acid, aniline was formed and gave an intense violet coloration with sodium hypochlorite solution. The appearance of benzene in the decomposition of the sulphonanilide compound is readily accounted for, seeing that Armstrong and Field (*Ber.*, 1874, **7**, 406) and Jacobsen (*Ber.*, 1876, **9**, 258) have shown that sulphonic acids are converted into the hydrocarbons by strong hydrochloric acid under pressure. The acid solution, after extracting with light petroleum, was made alkaline with sodium carbonate and distilled in steam. The distillate was extracted with ether, the ether removed, and the residue dehydrated in vacuo. A yellow oil weighing 0·8 gram remained. The substance did not solidify on introducing a crystal of *p*-chloraniline, even when cooled in ice; it yielded an acetyl derivative melting at 85—86° and a benzoyl derivative melting at 102°. This corresponds to *o*-chloraniline which was prepared from *o*-nitraniline, and then converted into the acetyl and benzoyl derivatives having the above melting points. In further confirmation, the *o*-chloraniline was heated with benzenesulphonic chloride and converted into the sulphonanilide melting at 129—130°, which agrees with the melting point of the product obtained by the action of sodium hypochlorite on benzenesulphonanilide. The reaction, therefore, probably occurs in two steps, as in the chlorination of the acetyl derivatives studied by Chattaway and Orton,

$$C_6H_5SO_2NHC_6H_5 + Cl_2 = C_6H_5SO_2{\cdot}NCl{\cdot}C_6H_5 + HCl,$$
$$C_6H_5SO_2{\cdot}NCl{\cdot}C_6H_5 = C_6H_5SO_2{\cdot}NH{\cdot}C_6H_4Cl,$$

with the formation mainly of benzenesulphonyl-*o*-chloranilide and a small quantity of the *p*-chloranilide.

Wallach (*Ber.*, 1877, **9**, 424) found that benzenesulphonanilide, when heated to 100° with phosphorus pentachloride, yields benzenesulphonyl *p*-chloranilide, m. p. 121°; but no reference is made to an *o*-compound. The authors have repeated Wallach's work, which they can confirm. The product is difficult to purify and only a small yield of pure substance could be obtained. From *p*-chloraniline and benzene sulphonic chloride the authors have also synthesised this substance, which melts at 121° as stated by Wallach.

To complete the series, the authors have synthesised the benzene sulphonyl-*m*-chloranilide from *m*-chloraniline, which has not been pre-

viously described; like the *p*-compound, it melts at 121°. It gave the following result on analysis:

0·2576 gave 12·85 c.c. moist nitrogen at 13° and 741 mm. N = 5·76.
$C_{12}H_{10}O_2NSCl$ requires N = 5·23 per cent.

The authors intend to continue the investigation.

180. "The relationship between the substitution and the constitution of benzeneazo-α-naphthol." By J. T. Hewitt and S. J. M. Auld.

Möhlau and Kegel (*Ber.*, 1900, 33, 2858) have shown that benzeneazo-α-naphthol reacts with Michler's hydrol (tetramethyldiaminobenzhydrol) to form a condensation product in the same manner as paraquinones and their derivatives. Moreover, the substance obtained acetylates in such a manner that the entering acetyl group attaches itself to a nitrogen atom. The authors mentioned draw the conclusion that benzeneazo-α-naphthol and its derivatives are of quinone-hydrazone type.

The results obtained by the authors of the present communication are in favour of an oxyazo-formula. Benzeneazo-α-naphthyl acetate yields aniline on complete fission and no acetanilide. By partial reduction, a hydrazo-compound is obtained melting about 160—165°; the formula $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_{10}H_6{\cdot}O{\cdot}COCH_3$ is confirmed by the insolubility of the substance in dilute alkalis.

Nitric acid is not a satisfactory substituting agent to use with benzeneazo-α-naphthol, but bromine reacts with the azonaphthol in presence of acetic acid and sodium acetate, forming a *monobromo*-derivative of m. p. 196°. This substance yields aniline on fission, the bromine therefore enters the naphthol nucleus. From this benzeneazobromonaphthol the *ethyl ether*, m. p. 220° (uncorr.), and *acetyl* derivative, m. p. 146°, have been prepared.

The following substances containing bromine in the benzene nucleus have been prepared for purposes of comparison.

o-*Bromobenzeneazo-α-naphthol*, m. p. 183°. o-*Bromobenzeneazo-α-naphthyl acetate*, m. p. 123°. m-*Bromobenzeneazo-α-naphthol*, m. p. 211° (uncorr.). m-*Bromobenzeneazo-α-naphthyl acetate*, m. p. 112°. *p*-Bromobenzeneazo-α-naphthol, m. p. 237—238° (Bamberger, *Ber.*, 1895, 28, 1896). p-*Bromobenzeneazo-α-naphthyl acetate*, m. p. 141°.

The bromination of benzeneazo-β-naphthol is now being studied.

ADDENDUM TO DISCUSSION

On Messrs. Hall and Plymen's paper, No. 162, on "The determination of available plant food in soils by the use of dilute solvents."

DR. DYER pointed out that any process must necessarily be empirical. The actions of the root sap of plants could not be exactly imitated and much must always depend, not only upon the composition of the solution used, but also upon its volume and the duration of contact. He was very glad that the 1 per cent. citric acid solution had on the whole given more reliable indications of the degree of comparative fertility as regarded both phosphoric acid and potash than did the other acid solutions tried. When he was in America a year ago, he found in use for the determination of "available" phosphoric acid a one-fifth normal solution of hydrochloric acid, but this did not give satisfactory results for potash and he understood that at that time they had not decided in America what was the best solution to use for potash. As to the limits which he had laid down as indicating need of manurial phosphoric acid or potash, both in his original paper on the Hoos Field soils and in a paper on the Broadbalk soils (*Phil. Trans.*, 1901, 194B., 235), he had pointed out that the limits which he gave related to cereal crops and might probably have to be modified with reference to root and other crops. In this direction, much more work was required. Dr. Dyer called attention to some experiments recently carried out by Mr. Ingle of the Yorkshire College, Leeds, in which he had extracted a large quantity of soil with 1 per cent. citric acid solution, and after washing out had grown various crops in it in pot-culture, with and without total or partial replacement of the constituents removed. Some of Mr. Ingle's photographs were exhibited, which showed that the soil when exhausted of its "available" constituents by 1 per cent. citric acid solution, was hardly able to support the life of bean plants, but that when the constituents thus dissolved out were replaced the plants flourished abundantly. Mr. Ingle's experiments were not yet completed, but so far they appeared to confirm the practical value of 1 per cent. citric acid solution as a reagent in soil analysis.

DR. J. A. VOELCKER remarked that the experiments of the authors had shown very clearly the influence of one constituent of the soil upon another. Mr. Hall had himself pointed out the variations caused by the presence or absence of lime, and Dr. Dyer had shown how the action of citric acid was influenced by the presence of sodium and magnesium salts, and how irregular were the results when farmyard manure had been applied to the land. He did not think it was right to take one particular solvent and of one particular strength, and

to apply it indiscriminately to all classes of soils alike, nor did he think that the use of hydrochloric acid should be abandoned on the grounds given. That a 1 per cent. solution showed, with certain soils, results not consistent with those of certain other solvents or with those of a strong solution of the acid afforded no proof that the acid was an unsuitable solvent. In work on which he had lately been engaged, he had found a 1 per cent. citric acid solution useful in many cases, and it was certainly an advance on the older methods, but he was not altogether satisfied with it as yet, and had not found the results to be in all cases consistent with the conclusions arrived at from practical experience of the land. It was not improbable that a distinction would have to be drawn between the two different classes of phosphoric acid present in the soil, the one the phosphoric acid naturally belonging to the soil, the other the phosphoric acid accumulated by repeated manurial applications.

ADDITIONS TO THE LIBRARY.

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Digest of criticisms on the United States Pharmacopœia, 1890. Part III. Pp. 180. Philadelphia. 1901.

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The next Ordinary Meeting of the Society will be held on Thursday, January 16th, at 8 p.m.

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